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ELECTRIC PROPAGATION ON LONG LINES TERMINATED BY LUMPED NETWORKS.

BY

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PART II. LINE INITIALLY NOT AT REST.

1. *Introduction:* This paper is a sequel to a previous paper [1] and extends the treatment to the case where the line is initially not at rest but has an arbitrary initial distribution of voltage and current. Such an initial distribution may be due to a lightning surge, to switching of arbitrary e.m.f.'s or to any other causes.

To the authors' knowledge this topic has not been dealt with previously in as general a form as is here given.[2] Hence no bibliography will be appended to this paper.

The notations here used are those of our previous paper.[1] Moreover many of the results of that paper are quoted here. Whenever equation or article numbers are preceded by "I,"

[1] See "Electric Propagation on Long Lines Terminated by Lumped Parameters," Part I, JOURNAL OF THE FRANKLIN INSTITUTE, Vol. 235 (1943), p. 41.

[2] Heaviside in his Electrical Papers, Vol. II, p. 382, gives expressions for propagation due to an impulsive excitation on an infinite line and states that he arrived at these expressions "very laboriously" and omits methods of arriving at them.

(Note—The Franklin Institute is not responsible for the statements and opinions advanced by contributors in the JOURNAL.)

it shall be understood that these numbers refer to that paper.

2. *Initial and Boundary Conditions for the Infinite Line:* Consider a line extending to infinity in both directions so that the boundary conditions are

$$\left.\begin{aligned} \lim_{x\to\infty} e(x,t) &= 0, \qquad \lim_{x\to\infty} i(x,t) = 0, \qquad (a)\\ \lim_{x\to-\infty} e(x,t) &= 0, \qquad \lim_{x\to-\infty} i(x,t) = 0. \qquad (b) \end{aligned}\right\} (2.1)$$

We shall assume that the initial conditions are:

$$\lim_{t\to 0+} e(x,t) = e_i(x) \text{ for all } x, \qquad \lim_{t\to 0+} i(x,t) = i_i(x) \text{ for all } x, \quad (2.2)$$

where $e_i(x)$ and $i_i(x)$ are given functions defined for $-\infty < x < +\infty$ and differentiable for all x. Moreover in order to be consistent with the boundary conditions (2.1), we shall assume that

$$\lim_{x\to\pm\infty} e_i(x) = 0, \qquad \lim_{x\to\pm\infty} i_i(x) = 0. \qquad (2.3)$$

3. *Transformed Solution for the Infinite Line:* Transforming the differential Eq. (I.2.1) by using (I.*A*.2) and the initial conditions (2.2) we have:

$$\left.\begin{aligned} -\frac{\partial E}{\partial x} &= (R + Lu)I - Li_i(x), \qquad (a)\\ -\frac{\partial I}{\partial x} &= (G + Cu)E - Ce_i(x). \qquad (b) \end{aligned}\right\} (3.1)$$

Transforming the boundary conditions (2.1) we have:

$$\lim_{x\to\pm\infty} E(x,u) = 0, \qquad \lim_{x\to\pm\infty} I(x,u) = 0. \qquad (3.2)$$

Eliminating I from (3.1a) and E from (3.1b) through differentiation we have:

$$\left.\begin{aligned} \frac{\partial^2 E}{\partial x^2} - \Lambda^2 E &= F_e(x,u), \qquad (a)\\ \frac{\partial^2 I}{\partial x^2} - \Lambda^2 I &= F_i(x,u), \qquad (b) \end{aligned}\right\} (3.3)$$

where

$$\left.\begin{aligned} F_e(x, u) &= -(R + Lu)Ce_i(x) + L\frac{di_i(x)}{dx}, \quad (a) \\ F_i(x, u) &= -(G + Cu)Li_i(x) + C\frac{de_i(x)}{dt}. \quad (b) \end{aligned}\right\} (3.4)$$

The solution of (3.3a) is (see, e.g., "A Treatise on Differential Equations," by A. R. Forsyth, p. 65):

$$E = \frac{1}{2\Lambda}\int_a^x F_e(y, u)\epsilon^{\Lambda(x-y)}dy - \frac{1}{2\Lambda}\int_b^x F_e(y, u)\epsilon^{-\Lambda(x-y)}dy. \quad (3.5)$$

Observe that as $x \to \infty$ the second integral in (3.5) becomes zero. Hence in order to satisfy (3.2), as $x \to +\infty$ the lower limit a in the first integral must be ∞. Similarly, as $x \to -\infty$ the first integral becomes zero. Hence in the second integral (3.5) the lower limit $b = -\infty$. Eq. (3.5) thus becomes:

$$E = -\frac{1}{2\Lambda}\left[\int_x^\infty F_e(y, u)\epsilon^{\Lambda(x-y)}dy + \int_{-\infty}^x F_e(y, u)\epsilon^{-\Lambda(x-y)}dy\right]. \quad (3.6)$$

Substitute in the first integral of (3.6) $x - y = -s$ and in the second integral $x - y = +s$ and obtain after combining both integrals

$$E = \frac{1}{2\Lambda}\int_0^\infty [F_e(x + s) + F_e(x - s)]\epsilon^{-\Lambda s}ds. \quad (3.7)$$

Substituting (3.4 in (3.7) and using (I.2.2) we have:

$$E(x, u) = \frac{CZ}{2}\int_0^\infty [e_i(x + s) + e_i(x - s)]\epsilon^{-\Lambda s}ds + \frac{L}{2}\int_0^\infty [-i_i(x + s) + i_i(x - s)]^{-\Lambda s}ds. \quad (3.8)$$

Proceeding in a similar manner and using Eq. (3.3b) we

have:

$$I(x, u) = \frac{C}{2}\int_0^{\infty} [-e_i(x+s) + e_i(x-s)]\epsilon^{-\Lambda s}ds + \frac{L}{2Z}\int_0^{\infty} [i_i(x+s) + i_2(x-s)]\epsilon^{-\Lambda s}ds. \quad (3.9)$$

Since we assumed that $e_i(x)$ and $i_i(x)$ converge to zero as $x \to \pm \infty$ the two integrals in (3.8) and (3.9) converge in some half plane where Ru is sufficiently large.

4. *Inversion of (3.8) and (3.9):* Refer to Art. (I.8) and observe that the expressions (3.8) and (3.9) comprise the factors $Z\epsilon^{-\Lambda s}$ and $(1/Z)\epsilon^{-\Lambda s}$ which can be inverted in a manner similar to that described there. Thus from (I.8.3) we have:

$$\left.\begin{aligned} L^{-1}[rZ\epsilon^{-\Lambda s} - \epsilon^{-(u+\rho)s/v}] &= \mathbf{1}(t - s/v)S_e(t, s/v), \quad s \geqq 0, \quad (a)\\ L^{-1}[\epsilon^{-\Lambda s} - \epsilon^{-(u+\rho)s/v}] &= \mathbf{1}(t - s/v)S_i(t, s/v), \quad s \geqq 0. \quad (b)\end{aligned}\right\} (4.1)$$

Now if we replace R, L, G, C respectively by G, C, R, L, then Λ, ρ, and v remain unchanged whereas Z, r, and σ become respectively $1/Z$, $1/r$, $-\sigma$. Hence Eq. (4.1a) becomes:

$$L^{-1}\left[\frac{1}{rZ}\epsilon^{-\Lambda s} - \epsilon^{-(u+\rho)s/v}\right] = \mathbf{1}(t - s/v)\bar{S}_e(t, s/v), \quad s \geqq 0, \quad (4.2)$$

where (see I.8.4):

$$\left.\begin{aligned} S_i(t, y) &= \sigma y\epsilon^{-\rho t}\frac{\mathfrak{I}_1(\sigma\sqrt{t^2 - y^2})}{\sqrt{t^2 - y^2}}, \quad (a)\\ S_e(t, y) &= \sigma\epsilon^{-\rho t}\left[\frac{t}{\sqrt{t^2 - y^2}}\mathfrak{I}_1(\sigma\sqrt{t^2 - y^2}) + \mathfrak{I}_0(\sigma\sqrt{t^2 - y^2})\right], \quad (b)\\ \bar{S}_e(t, y) &= -\sigma\epsilon^{-\rho t}\left[\frac{t}{\sqrt{t^2 - y^2}}\mathfrak{I}_1(-\sigma\sqrt{t^2 - y^2}) + \mathfrak{I}_0(-\sigma\sqrt{t^2 - y^2})\right]\\ &= \sigma\epsilon^{-\rho t}\left[\frac{t}{\sqrt{t^2 - y^2}}\mathfrak{I}_1(\sigma\sqrt{t^2 - y^2}) - \mathfrak{I}_0(\sigma\sqrt{t^2 - y^2})\right]. \quad (c)\end{aligned}\right\} (4.3)$$

Now the inversions of $E(x, u)$ and $I(x, u)$ involve the inversion of integrals whose integrands have the form $\epsilon^{-\Delta s}\phi(s)$. To invert these integrals consider (4.1*b*), multiply it by $\phi(s)$ and integrate with respect to s:

$$\left.\begin{aligned} L^{-1}\left[\int_0^\infty \epsilon^{-\Delta s}\phi(s)ds\right] - L^{-1}\left[\int_0^\infty \epsilon^{-(u+\rho)s/v}\phi(s)ds\right] & \\ = \int_0^\infty \mathbf{1}(t - s/v)S_i(t, s/v)\phi(s)ds, & \quad (a) \\ = \int_0^{vt} S_i(t, s/v)\phi(s)ds, & \quad (b) \\ = v\int_0^t S_i(t, \tau)\phi(v\tau)d\tau. & \quad (c) \end{aligned}\right\} (4.4)$$

In order to evaluate the second inverse on the left of (4.4) proceed as follows:

$$L^{-1}\left[\frac{1}{u}\epsilon^{-us/v}\right] = \mathbf{1}(t - s/v). \tag{4.5}$$

Multiply both sides of (4.5) by $\epsilon^{-\rho(s/v)}\phi(s)$ and integrate with respect to s and obtain after interchanging the order of integration:

$$\left.\begin{aligned} L^{-1}\left[\frac{1}{u}\int_0^\infty \epsilon^{-(u+\rho)s/v}\phi(s)ds\right. & \\ = \int_0^\infty \mathbf{1}(t - s/v)\epsilon^{-\rho s/v}\phi(s)ds, & \quad (a) \\ = \int_0^{vt} \epsilon^{-\rho s/v}\phi(s)ds. & \quad (b) \end{aligned}\right\} (4.6)$$

But the right hand side of (4.6) is zero for $t = 0$; hence by (I.*A*.2):

$$\left.\begin{aligned} L^{-1}\left[\int_0^\infty \epsilon^{-(u+\rho)s/v}\phi(s)ds\right] = \frac{d}{dt}\int_0^{vt} \epsilon^{-\rho s/v}\phi(s)ds, & \quad (a) \\ = v\epsilon^{-\rho t}\phi(vt). & \quad (b) \end{aligned}\right\} (4.7)$$

Using (4.7*b*) and (4.4*c*) in (4.4*a*) we have:

$$L^{-1}\left[\int_0^\infty \epsilon^{-\Delta s}\phi(s)ds\right] = v\left[\epsilon^{-\rho t}\phi(vt) + \int_0^t S_i(t, \tau)\phi(v\tau)d\tau\right]. \tag{4.8}$$

Apply the same procedure to (4.1*a*) and (4.2) and obtain:

$$\left.\begin{aligned} L^{-1}\left[Z\int_0^{\infty} \epsilon^{-\Delta s}\phi(s)ds \right] &= \frac{v}{r}\left[\epsilon^{-\rho t}\phi(vt) + \int_0^t S_e(t,\tau)\phi(v\tau)d\tau \right], \quad (a) \\ L^{-1}\left[\frac{1}{Z}\int_0^{\infty} \epsilon^{-\Delta s}\phi(s)ds \right] &= rv\left[\epsilon^{-\rho t}\phi(vt) + \int_0^t \bar{S}_e(t,\tau)\phi(v\tau)d\tau \right]. \quad (b) \end{aligned}\right\} (4.9)$$

If we substitute (4.3) in (4.8) and (4.9) we encounter expressions of the following form:

$$\left.\begin{aligned} \mathfrak{S}_i[\phi;t] &= \phi(t) + \sigma\int_0^t \tau\,\frac{\mathfrak{J}_1(\sigma\sqrt{t^2-\tau^2})}{\sqrt{t^2-\tau^2}}\,\phi(\tau)d\tau, \quad (a) \\ \mathfrak{S}_e[\phi;t] &= \phi(t) + \sigma\int_0^t \left[\frac{t}{\sqrt{t^2-\tau^2}}\,\mathfrak{J}_1(\sigma\sqrt{t^2-\tau^2}) + \mathfrak{J}_0(\sigma\sqrt{t^2-\tau^2}) \right]\phi(\tau)d\tau, \quad (b) \\ \bar{\mathfrak{S}}_e[\phi;t] &= \phi(t) + \sigma\int_0^t \left[\frac{t}{\sqrt{t^2-\tau^2}}\,\mathfrak{J}_1(\sigma\sqrt{t^2-\tau^2}) - \mathfrak{J}_0(\sigma\sqrt{t^2-\tau^2}) \right]\phi(\tau)d\tau. \quad (c) \end{aligned}\right\} (4.10)^*$$

We shall call $\mathfrak{S}_i$, $\mathfrak{S}_e$ and $\bar{\mathfrak{S}}_e$ the distortion operators. Expand these operators in powers of σ and obtain:

$$\left.\begin{aligned} \mathfrak{S}_i[\phi;t] &= \phi(t) + ((\sigma^2)), \quad (a) \\ \mathfrak{S}_e[\phi;t] &= \phi(t) + \sigma\int_0^t \phi(\tau)d\tau + ((\sigma^2)), \quad (b) \\ \bar{\mathfrak{S}}_e[\phi;t] &= \phi(t) - \sigma\int_0^t \phi(\tau)d\tau + ((\sigma^2)). \quad (c) \end{aligned}\right\} (4.11)^*$$

Substituting (4.3) in (4.8) and (4.9), and using (4.10) we have:

$$\left.\begin{aligned} L^{-1}\left[\int_0^\infty \epsilon^{-\Delta s}\phi(s)ds\right] &= v\epsilon^{-\rho t}\mathfrak{S}_i[\phi(v\tau);t], && (a)\\ L^{-1}\left[Z\int_0^\infty \epsilon^{-\Delta s}\phi(s)ds\right] &= \frac{1}{C}\epsilon^{-\rho t}\mathfrak{S}_e[\phi(v\tau);t], && (b)\\ L^{-1}\left[\frac{1}{Z}\int_0^\infty \epsilon^{-\Delta s}\phi(s)ds\right] &= \frac{1}{L}\epsilon^{-\rho t}\overline{\mathfrak{S}}_e[\phi(v\tau);t], && (c) \end{aligned}\right\} (4.12)$$

where $1/C = v/r$ and $1/L = rv$ (see I.2.2).

Substitute (4.12) in (3.8) and (3.9), and obtain:

$$\left.\begin{aligned} e_{\pm\alpha}(x,t) &= L^{-1}[E(x,u)]\\ &= \tfrac{1}{2}\epsilon^{-\rho t}\{\mathfrak{S}_e[e_i(x+v\tau)+e_i(x-v\tau);t]\\ &\quad + r\mathfrak{S}_i[-i_i(x+v\tau)+i_i(x-v\tau);t]\}, && (a)\\ i_{\pm\alpha}(x,t) &= L^{-1}[I(x,u)]\\ &= \tfrac{1}{2}\epsilon^{-\rho t}\left\{\frac{1}{r}\mathfrak{S}_i[-e_i(x+v\tau)+e_i(x-v\tau);t]\right.\\ &\quad \left. + \overline{\mathfrak{S}}_e[i_i(x+v\tau)+i_i(x-v\tau);t]\right\}. && (b) \end{aligned}\right\} (4.13)^*$$

5. *Eqs. (4.13) are Solutions of the Infinite Line Problem:* That (4.13) are not only inverses of $E(x,u)$ and $I(x,u)$ but are solutions of the infinite line problem may be shown as follows:

a. We recall that e_i and i_i are assumed to be differentiable (see Art. 2). Differentiating (4.13) with respect to x and t and substituting in (I.2.1) we find that (4.13) satisfy these differential equations.

b. As to the initial conditions (2.2), observe that by (4.10):

$$\mathfrak{S}_i[\phi;0] = \mathfrak{S}_e[\phi;0] = \overline{\mathfrak{S}}_e[\phi;0] = \phi(0). \qquad (5.1)$$

Substituting (5.1) in (4.13) we have:

$$\left.\begin{aligned} \lim_{t\to 0+} e_{\pm\alpha}(x,t) &= \tfrac{1}{2}[e_i(x)+e_i(x)]\\ &\quad + \frac{r}{2}[-i_i(x)+i_i(x)] = e_i(x), && (a)\\ \lim_{t\to 0+} i_{\pm\alpha}(x,t) &= \frac{1}{2r}[-e_i(x)+e_i(x)]\\ &\quad + \tfrac{1}{2}[i_i(x)+i_i(x)] = i_i(x). && (b) \end{aligned}\right\} (5.2)$$

c. As to the boundary conditions (2.1) we recall, by (2.3), that $e_i(x)$ and $i_i(x)$ converge to 0 as $x \to \pm \infty$. Hence $e_i(x \pm v\tau)$ and $i_i(x \pm v\tau)$ converge to 0, as $x \to \pm \infty$, uniformly with respect to τ in any finite interval $0 \leqq \tau \leqq t$. Thus by (4.10) the functions $\mathfrak{S}[e_i(x \pm v\tau); t]$ and $\mathfrak{S}[i_i(x \pm v\tau); t]$ also converge to zero as $x \to \pm \infty$.

The functions (4.13) therefore satisfy the differential equations as well as the boundary conditions and are, therefore, solutions of our problem.

Using (4.11) in (4.13) we obtain the following expansion of e and i in powers of σ:

$$\left.\begin{aligned} e_{\pm\infty}(x,t) &= \tfrac{1}{2}\epsilon^{-\rho t}\big[e_i(x+vt) + e_i(x-vt) \\ &\quad - ri_i(x+vt) + ri_i(x-vt) \\ &\quad + \sigma\int_0^t \{e_i(x+v\tau) + e_i(x-v\tau)\}d\tau\big] + ((\sigma^2)), \quad (a) \\ i_{\pm\infty}(x,t) &= \tfrac{1}{2}\epsilon^{-\rho t}\Big[-\frac{1}{r}e_i(x+vt) + \frac{1}{r}e_i(x-vt) \\ &\quad + i_i(x+vt) + i_i(x-vt) \\ &\quad - \sigma\int_0^t \{i_i(x+v\tau) + i_i(x-v\tau)\}d\tau\big] + ((\sigma^2)). \quad (b) \end{aligned}\right\} (5.3)$$

6. *The Finite Line: a. Initial and Boundary Conditions.* For the line of finite length s, we replace the boundary conditions (2.1) by the boundary conditions (I.4.1) and (I.4.5) which are:

$$\left.\begin{aligned} D_1e(o,t) + D_2i(o,t) &= D_0e_0(t), \quad (a) \\ D_{1s}e(s,t) - D_{2s}i(s,t) &= 0. \quad (b) \end{aligned}\right\} (6.1)$$

It will be further understood that the assumptions made in Art. (I.4) regarding D_0, D_1, D_2, D_{1s}, D_{2s} and $e_0(t)$ also hold here.

Again, the initial conditions (2.2) will now hold in the interval $0 \leqq x \leqq s$ instead of for all x. We shall further assume that $e_i(x)$ has N_1 derivatives, that $i_i(x)$ has N_2 derivatives, for $0 \leqq x \leqq s$, where $N_1 \geqq n_1$ and n_{1s}, $N_2 \geqq n_2$ and n_{2s}.

Finally $e_i(x)$ and $i_i(x)$ shall be continued beyond the inter-

val $0 \leqq x \leqq s$ in any arbitrary manner provided that:

$e_i(x)$ shall have N_1 derivatives for $-\infty < x < +\infty$,
and $\lim_{x \to \pm\infty} e_i(x) = 0$,

$i_i(x)$ shall have N_2 derivatives for $-\infty < x < +\infty$,
and $\lim_{x \to \pm\infty} i_i(x) = 0$.

b. Solution: In obtaining the solution of the finite line problem we shall first solve a problem involving an initially-excited infinite line and then solve another problem involving an initially-at-rest finite line. By adding these two solutions we obtain the desired solution of the initially excited finite line problem.

For the initially-excited infinite line consider $e_1(x)$ and $i_1(x)$ to be as defined above in the interval $-\infty < x < +\infty$ and solve the problem as in Art. 3. Let the solutions be $e_1(x, t)$ and $i_1(x, t)$. With e_1 and i_1 known, form the functions e_{01} and e_{s1} as follows:

$$\left.\begin{aligned} e_{01}(t) &= -D_1 e_1(o, t) - D_2 i_1(o, t), \quad t \geqq 0, \quad (a) \\ e_{s1}(t) &= -D_{1s} e_1(s, t) + D_{2s} i_1(s, t), \quad t \geqq 0. \quad (b) \end{aligned}\right\} (6.2)$$

Observe that all the derivatives occurring in (6.2) exist because of the assumptions made regarding e_i and i_i which enter into the solutions e_1 and i_1.

For the initially-at-rest finite line, consider $e_2(x, t)$ and $i_2(x, t)$ to be solutions which satisfy the following boundary conditions:

$$\left.\begin{aligned} D_1 e_2(o, t) + D_2 i_2(o, t) &= D_0 e_0(t) + e_{01}(t), \quad (a) \\ D_{1s} e_2(s, t) - D_{2s} i_2(s, t) &= e_{s1}(t). \quad (b) \end{aligned}\right\} (6.3)$$

The solutions e_2 and i_2 can be obtained as in Art. I.12.

We now maintain that

$$\left.\begin{aligned} e(x, t) &= e_1(x, t) + e_2(x, t), \quad (a) \\ i(x, t) &= i_1(x, t) + i_2(x, t), \quad (b) \end{aligned}\right\} (6.4)^*$$

are solutions of our problem. To prove this statement we have to show that (6.4) satisfy the differential equations (I.2.1)

as well as the initial conditions (2.2) and boundary conditions (6.1).

Since both e_1, i_1 and e_2, i_2 satisfy the differential Eqs. (2.1) their sum does. Hence (6.4) satisfy (2.1).

To show that (6.4) satisfy (2.2) write:

$$\left.\begin{aligned} \lim_{t\to 0+} e(x,t) &= \lim_{t\to 0+} e_1(x,t) + \lim_{t\to 0+} e_2(x,t) \\ &= e_i(x) + 0, \qquad (a) \\ \lim_{t\to 0+} i(x,t) &= \lim_{t\to 0+} i_1(x,t) + \lim_{t\to 0+} i_2(x,t) \\ &= i_i(x) + 0. \qquad (b) \end{aligned}\right\} (6.5)$$

Finally to show that (6.4) satisfy (6.1) substitute (6.2), (6.3) and (6.4) in (6.1), obtaining:

$$\left.\begin{aligned} D_1 e(o,t) + D_2 i(o,t) &= D_1 e_1(o,t) + D_2 i_1(o,t) \\ &\quad + D_1 e_2(o,t) + D_2 i_2(o,t) \\ &= -e_{01}(t) + D_0 e_0(t) + e_{01}(t) \\ &= D_0 e_0(t), \qquad (a) \\ D_{1s} e(s,t) - D_{2s} i(s,t) &= D_{1s} e_1(s,t) - D_{2s} i_1(s,t) \\ &\quad + D_{1s} e_2(s,t) - D_{2s} i_2(s,t) \\ &= -e_{s1}(t) + e_{s1}(t) = 0. \qquad (b) \end{aligned}\right\} (6.6)$$

7. *Application to an Impulsive Disturbance on an Infinite Line:* Imagine a voltage impulse of moment M_0 to occur at a point $x = x_0$ of an infinite line. We shall divide the solution into two parts considering first the distortionless line and next the distortive line.

Let the infinite line have the following initial conditions:

$$\left.\begin{aligned} e(x,o) &= \begin{cases} e_i(x) & -\delta < x - x_0 < \delta, \\ 0 & |x - x_0| \geqq \delta, \end{cases} \qquad (a) \\ i(x,o) &= i_i(x) = 0, \qquad -\infty < x < +\infty, \qquad (b) \end{aligned}\right\} (7.1)$$

where $e_i(x)$ is any arbitrary function differentiable for all x and where

$$\int_{x_0-\delta}^{x_0+\delta} e_i(x)dx = M_0. \qquad (7.2)$$

We shall solve the problem for $e(x, t)$ and $i(x, t)$, assuming that $\delta \to 0$ with M_0 remaining fixed. In other words, we have a voltage impulse of moment M_0. We shall consider the solution under two headings: (a_1) the distortionless line and (a_2) the distortive line.

a_1. *Distortionless line* ($\sigma = 0$): Substitute (7.1) in (5.3) and obtain, as $\delta \to 0$, and $\sigma = 0$:

$$\left.\begin{aligned} e_{\pm\alpha}(x, t) &= 0 \quad \text{if} \quad x \pm vt \neq x_0 \quad \therefore \quad x \neq x_0 \pm vt, \quad (a) \\ i_{\pm\alpha}(x, t) &= 0 \quad \text{if} \quad x \pm vt \neq x_0 \quad \therefore \quad x \neq x_0 \pm vt, \quad (b) \end{aligned}\right\} (7.3)$$

whereas at $x = x_0 \pm vt$

$$\left.\begin{aligned} &\lim_{\delta \to 0} \int_{x_0 + vt - \delta}^{x_0 + vt + \delta} e_{\pm\alpha}(x, t)dx \\ &\qquad = \lim_{\delta \to 0} \int_{x_0 - vt - \delta}^{x_0 - vt + \delta} e_{\pm\alpha}(x, t)dx = \tfrac{1}{2}\epsilon^{-\rho t} M_0, \quad (a) \\ &\lim_{\delta \to 0} \int_{x_0 + vt - \delta}^{x_0 + vt + \delta} i_{\pm\alpha}(x, t)dx \\ &\qquad = -\lim_{\delta \to 0} \int_{x_0 - vt - \delta}^{x_0 - vt + \delta} i_{\pm\alpha}(x, t)dx = \frac{1}{2r}\epsilon^{-\rho t} M_0. \quad (b) \end{aligned}\right\} (7.4)^*$$

Now observe that voltage and current occur on the line only at points $x = x_0 \pm vt$. Hence we have a propagation of voltage and current from the point x_0 in both directions with a velocity v. The given voltage impulse of moment M_0 divides into two equal parts propagating in either direction from the point x_0, the moment at any time t being $\frac{1}{2}\epsilon^{-\rho t} M_0$. This voltage impulse also gives rise to two current impulses (equal in magnitude but opposite in sign) which also propagate in either direction from x_0 at the same velocity, the moment at any time t being $\frac{1}{2r}\epsilon^{-\rho t} M_0$.

a_2. *Distortive Line* ($\sigma \neq 0$): Since here $\sigma \neq 0$ we use Eqs. (4.13) in investigating the behavior of the line. Again, by (7.1), $i_i(x) = 0$. Hence only terms involving e_i in (4.13) need be considered. Substitute (4.3) in (4.10) and the result

in (4.13) and obtain as one of the terms:

$$\lim_{\delta \to 0} \epsilon^{-\rho t} \mathfrak{S}_e[e_i(x + v\tau); t] = \lim_{\delta \to 0} \left[\epsilon^{-\rho t} e_i(x + vt) + \int_0^t S_e(t, \tau) e_i(x + v\tau) d\tau \right]. \quad (7.5)$$

Observe that $e_i(x + vt) \not\equiv 0$ only when $x_0 - \delta \leqq x + v\tau \leqq x_0 + \delta$. That is, only when

$$\frac{x_0 - x - \delta}{v} \leqq \tau \leqq \frac{x_0 - x + \delta}{v}. \quad (7.6)$$

Hence the integral in (7.5) is not zero only when

$$0 < (x_0 - x)/v < t. \quad (7.7)$$

We thus have two cases of (7.5) to consider:

(1) if $t < \dfrac{x_0 - x}{v}$ then (7.5) becomes:

$$\lim_{\delta \to 0} \epsilon^{-\rho t} \mathfrak{S}_e[e_i(x + v\tau); t] = \lim_{\delta \to 0} \epsilon^{-\rho t} e_i(x + vt) + 0 = 0, \quad (7.8)$$

(2) if $0 < (x_0 - x)/v < t$ then (7.5) becomes:

$$\left.\begin{aligned}
&\lim_{\delta \to 0} \epsilon^{-\rho t} \mathfrak{S}_e[e_i(x + v\tau); t] \\
&= \lim_{\delta \to 0} \Bigg[\epsilon^{-\rho t} e_i(x + vt) \\
&\qquad + \int_{(x_0 - x - \delta)/v}^{(x_0 - x + \delta)/v} S_e(t, \tau) e_i(x + v\tau) d\tau \Bigg], \quad (a) \\
&= \lim_{\delta \to 0} \epsilon^{-\rho t} e_i(x + vt) \\
&\quad + S_e\left(t, \frac{x_0 - x}{v}\right) \lim_{\delta \to 0} \int_{(x_0 - x - \delta)/v}^{(x_0 - x + \delta)/v} e_i(x + v\tau) d\tau, \quad (b) \\
&= \lim_{\delta \to 0} \epsilon^{-\rho t} e_i(x + vt) \\
&\qquad + S_e\left(t, \frac{x_0 - x}{v}\right) \lim_{\delta \to 0} \frac{1}{v} \int_{x_0 - \delta}^{x_0 + \delta} e_i(y) dy, \quad (c) \\
&= \lim_{\delta \to 0} \epsilon^{-\rho t} e_i(x + vt) + \frac{M_0}{v} S_e\left(t, \frac{x_0 - x}{v}\right). \quad (d)
\end{aligned}\right\} (7.9)$$

Hence

$$\operatorname*{Lim}_{\delta\to 0} \epsilon^{-\rho t}\mathfrak{S}_e[e_i(x+v\tau);t] = \frac{M_0}{v} S_e\left(t, \frac{x_0-x}{v}\right). \quad (7.10)$$

In the same way

$$\left.\begin{aligned} &\operatorname*{Lim}_{\delta\to 0} \epsilon^{-\rho t}\mathfrak{S}_e[e_i(x-v\tau);t] \\ &\quad = 0 \quad \text{if} \quad t < (x-x_0)/v, \qquad (a) \\ &\quad = \frac{M_0}{v} S_e\left(t, \frac{x-x_0}{v}\right) \quad \text{if} \quad 0 < \frac{x-x_0}{v} < t, \qquad (b) \end{aligned}\right\} (7.11)$$

$$\left.\begin{aligned} &\operatorname*{Lim}_{\delta\to 0} \epsilon^{-\rho t}\mathfrak{S}_i[e_i(x+v\tau);t] \\ &\quad = 0 \quad \text{if} \quad t < (x_0-x)/v, \qquad (a) \\ &\quad = \frac{M_0}{v} S_i\left(t; \frac{x_0-x}{v}\right) \quad \text{if} \quad 0 < \frac{x_0-x}{v} < t, \qquad (b) \end{aligned}\right\} (7.12)$$

$$\left.\begin{aligned} &\operatorname*{Lim}_{\delta\to 0} \epsilon^{-\rho t}\mathfrak{S}_i[e_i(x-v\tau);t] \\ &\quad = 0 \quad \text{if} \quad t < (x-x_0)/v, \qquad (a) \\ &\quad = \frac{M_0}{v} S_i\left(t, \frac{x-x_0}{v}\right) \quad \text{if} \quad 0 < \frac{x-x_0}{v} < t. \qquad (b) \end{aligned}\right\} (7.13)$$

On the other hand at $x = x_0 \pm vt$:

$$\left.\begin{aligned} &\operatorname*{Lim}_{\delta\to 0} \int_{x_0\pm vt-\delta}^{x_0\pm vt+\delta} \epsilon^{-\rho t}\mathfrak{S}_e[e_i(x\mp y\tau);t]dx \\ &\quad = \operatorname*{Lim}_{\delta\to 0}\left[\int_{x_0\pm vt-\delta}^{x_0\pm vt+\delta} \epsilon^{-\rho t} e_i(x\mp vt)dx\right. \\ &\qquad \left. + \frac{M_0}{v}\int_{x_0\pm vt-\delta}^{x_0\pm vt+\delta} S_e\left(t, \mp\frac{x_0-x}{v}\right)dx\right], \qquad (a) \\ &\quad = \epsilon^{-\rho t} M_0 + 0. \qquad (b) \end{aligned}\right\} (7.14)$$

Similarly:

$$\operatorname*{Lim}_{\delta\to 0} \int_{x_0\pm vt-\delta}^{x_0\pm vt+\delta} \epsilon^{-\rho t}\mathfrak{S}_i[e_i(x\mp v\tau);t]dx = \epsilon^{-\rho t} M_0. \quad (7.15)$$

Substitute (7.8) to (7.15) in (4.13) and obtain

$$\left.\begin{aligned} e_{\pm\alpha}(x,t) &= 0 \quad \text{if} \quad 0 \leqq t < |x-x_0|/v, && (a)\\ &= \frac{M_0}{v} S_e(t,o) \quad \text{if} \quad x = x_0, && (b)\\ &= \frac{M_0}{2v} S_e\left(t, \frac{|x-x_0|}{v}\right) \\ &\qquad \text{if} \quad 0 < \frac{|x-x_0|}{v} < t, && (c) \end{aligned}\right\} (7.16)^*$$

$$\left.\begin{aligned} i_{\pm\alpha}(x,t) &= 0 \quad \text{if} \quad 0 \leqq t < |x-x_0|/v, && (a)\\ &= 0 \quad \text{if} \quad x = x_0, && (b)\\ &= \pm \frac{1}{2r}\frac{M_0}{v} S_i\left(t, \frac{|x-x_0|}{v}\right) \\ &\qquad \text{if} \quad 0 < \frac{|x-x_0|}{v} < t, && (c) \end{aligned}\right\} (7.17)^*$$

whereas at $x = x_0 \pm vt$ we have

$$\left.\begin{aligned} &\lim_{\delta\to 0} \int_{x_0+vt-\delta}^{x_0+vt+\delta} e_{\pm\alpha}(x,t)dx \\ &\qquad = \lim_{\delta\to 0} \int_{x_0-vt-\delta}^{x_0-vt+\delta} e_{\pm\alpha}(x,t)dx = \frac{M_0}{2}\epsilon^{-\rho t}, && (a)\\ &\lim_{\delta\to 0} \int_{x_0+vt-\delta}^{x_0+vt+\delta} i_{\pm\alpha}(x,t)dx \\ &\qquad = -\lim_{\delta\to 0} \int_{x_0-vt-\delta}^{x_0-vt+\delta} i_{\pm\alpha}(x,t)dx = \frac{M_0}{2r}\epsilon^{-\rho t}. && (b) \end{aligned}\right\} (7.18)^*$$

Eqs. (7.16), (7.17) and (7.18) state that at any point $x \neq x_0$ there exists voltage and current disturbances only for $t \geqq |x-x_0|/v$. Hence there is a propagation of voltage and current from the point x_0 in both directions with the velocity v. The given voltage impulse of moment M_0 divides into two equal parts propagating in either direction from the point x_0, the moment at any time being $\frac{M_0}{2}\epsilon^{-\rho t}$. This voltage impulse gives rise to two current impulses of equal magnitude but

opposite sign, which propagate in either direction from x_0 at the same velocity. Their moment is $\frac{M_0}{2r}\epsilon^{-\rho t}$. The difference between the distortionless and distortive line is that, whereas in the distortionless line there exists voltage and current only at the instant $t = |x - x_0|/v$, in the distortive line there exists voltage and current for all instants $t \geqq |x - x_0|/v$. That part of the voltage and current which is observed at $t > |x - x_0|/v$ shall be called the "afterflow" or "tail." With this definition of tail we might state that the difference between a distortive and distortionless line is that in the former a tail exists while in the latter it does not. The tail (see 7.16*b*) of voltage at $x = x_0$ is $(M_0/v)S_e(t, o)$ and at the point $x \neq x_0$ (see 7.16*c*) it is $(M_0/2v)S_e(t, |x - x_0|/v)$. The tail of current (see 7.17*b*) at $x = x_0$ is zero and at a point $x \neq x_0$ (see 7.17*c*) it is $\pm (M_0/2rv)S_i(t, |x - x_0|/v)$.

Let us investigate more closely the nature of the tail. The tail of the voltage is (see 7.16):

$$\left.\begin{aligned} e_a(x, t) &= \frac{M_0}{v} S_e(t, o) \quad \text{if} \quad x = x_0, \qquad (a) \\ &= \frac{M_0}{2v} S_e(t, |x - x_0|/v) \quad \text{if} \quad x \neq x_0. \qquad (b) \end{aligned}\right\} (7.19)$$

Substitute (4.3*b*) in (7.19*a*) and obtain:

$$e_a(x_0, t) = (\sigma M_0/v)\epsilon^{-\rho t}[I_0(\sigma t) + I_1(\sigma t)]. \qquad (7.20)$$

Expand (7.20) in powers of t and obtain:

$$e_a(x_0, t) = (\sigma M_0/v)\left[1 - \left(\rho - \frac{\sigma}{2}\right)t + ((t^2))\right], \qquad (7.21)$$

which shows that the tail decreases the more rapidly the greater is $\rho - \sigma/2 = \frac{1}{2}R/L + G/C$. Since for large positive y, asymptotically

$$I_0(y) \approx I_1(y) \approx (2\pi y)^{-1/2}\epsilon^{y}, \qquad (7.22)$$

Eq. (7.20) gives for large t, asymptotically:

$$e_a(x_0, t) \approx (\sigma M_0/v)(2\pi\sigma t)^{-1/2}\epsilon^{(\sigma-\rho)t} = (M_0/v)\sqrt{\sigma/2\pi t}\,\epsilon^{-(G/C)t}. \qquad (7.23)$$

Obviously for large t the tail decreases rapidly if G/C is large, but very slowly if G/C is nearly zero. Hence one may expect the tail to last for a long time if the conductance of the line is small.

In order to plot the tail for any line we introduce the dimensionless quantities:

$$\left.\begin{aligned} t' &= \sigma t, && (a)\\ x' &= (\sigma/v)(x - x_0), && (b)\\ e'_a &= (v/\sigma M_0)e_a. && (c) \end{aligned}\right\} (7.24)$$

Substitute (4.3b) in (7.19) and use (7.24) in the result, thereby obtaining:

$$\left.\begin{aligned} e_a'(x', t') &= \tfrac{1}{2}\epsilon^{-(\rho/\sigma)t'}\left[I_0(\sqrt{t'^2 - x'^2}) + \frac{t'}{\sqrt{t'^2 - x'^2}} I_1(\sqrt{t'^2 - x'^2}) \right] \\ &\qquad \text{if} \quad x' \neq 0, \quad (a)\\ &= \epsilon^{-(\rho/\sigma)t'}[I_0(t') + I_1(t')] \quad \text{if} \quad x' = 0. \quad (b) \end{aligned}\right\} (7.25)$$

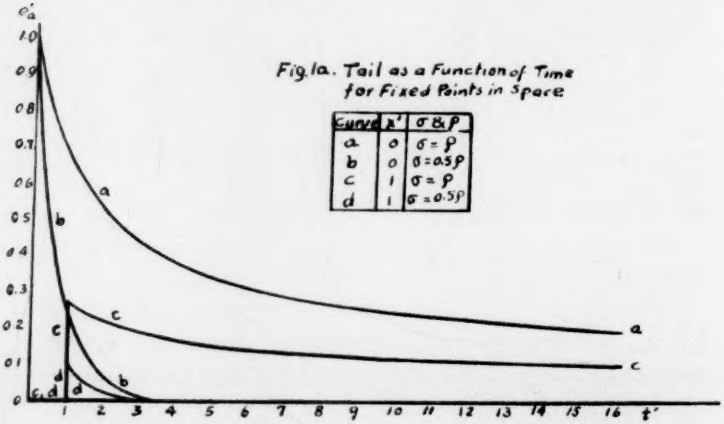

Fig. 1a. Tail as a Function of Time for Fixed Points in Space

Curve	x'	σ & ρ
a	0	σ = ρ
b	0	σ = 0.5ρ
c	1	σ = ρ
d	1	σ = 0.5ρ

FIG. 1a. Tail as a function of time for fixed points in space.

Eqs. (7.25) are plotted in Figs. 1 for the cases $\sigma = \rho$ (that is $G = 0$), $\sigma = 0.5\rho$ (that is large G), and for several fixed values of x' and t'.

8. *Application to an Impulsive Disturbance on a Finite Line:* Consider the illustrative problem of Art. I.16 and imagine the voltage impulse (7.2) to occur at a point $x = x_0 > 0$.

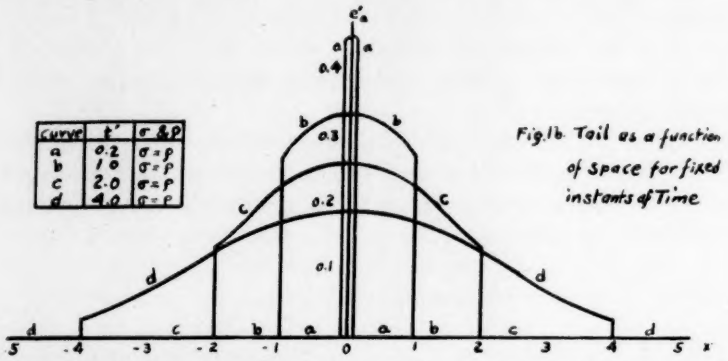

FIG. 1*b*. Tail as a function of space for fixed instants of time.

Referring to (6.2) observe that $e_1(x, t)$ and $i_1(x, t)$ were found in Art. 7 (Eqs. 7.16 and 7.17). In particular, we have:

$$\left.\begin{aligned} e_1(o, t) &= 0 \quad \text{if} \quad o \leqq t < x_0/v, && (a)\\ &= \frac{M_0}{2v} S_e(t, x_0/v) \quad \text{if} \quad o < x_0/v < t, && (b) \end{aligned}\right\} (8.1)$$

$$\left.\begin{aligned} i_1(o, t) &= 0 \quad \text{if} \quad o \leqq t < x_0/v, && (a)\\ &= -\frac{M_0}{2rv} S_i(t, x_0/v) \quad \text{if} \quad o < x_0/v < t, && (b) \end{aligned}\right\} (8.2)$$

$$\left.\begin{aligned} e_1(s, t) &= 0 \quad \text{if} \quad o \leqq t < (s - x_0)/v, && (a)\\ &= \frac{M_0}{2v} S_e[t, (s - x_0)/v] && \\ &\qquad \text{if} \quad o < (s - x_0)/v < t, && (b) \end{aligned}\right\} (8.3)$$

$$\left.\begin{aligned} i_1(s, t) &= 0 \quad \text{if} \quad o \leqq t < (s - x_0)/v, && (a)\\ &= +\frac{M_0}{2rv} S_i[t, (s - x_0)/v] && \\ &\qquad \text{if} \quad o < (s - x_0)/v < t. && (b) \end{aligned}\right\} (8.4)$$

D_1, D_2, D_{1s}, and D_{2s} are given in (I.16.4) and (I.16.8). The substitution of these values of the D's along with (8.1) to (8.4) in (6.2) gives $e_{o1}(t)$ and $e_{s1}(t)$.

Next substitute $e_{o1}(t)$ and $e_{s1}(t)$ in (6.3) and follow the procedure of Art. I (12) thereby obtaining e_2 and i_2.

Use these values of e_2 and i_2 along with the values of e_1 and i_1 from (7.16) and (7.17) in (6.4) and obtain the solution of the finite line.

Naturally this is a mere outline of the procedure. The actual work involves too much detail to be worked out in this paper and adds nothing new to the methods which are fully illustrated in Art. I (12).

RATES OF EVAPORATION OF WATER THROUGH COMPRESSED MONOLAYERS ON WATER.*

BY

IRVING LANGMUIR AND VINCENT J. SCHAEFER.

Rideal [1] was unable to detect any decrease in the rate of evaporation of water in open dishes in air at atmospheric pressure when the water was covered with a monolayer of stearic or oleic acid. However, the evaporation in vacuum from one leg of an inverted U tube at 25° C. into the other leg at 0° was reduced about 25 per cent. by a film of stearic acid and 50 per cent. by oleic acid.

It was found later by Langmuir and Langmuir [2] that even at atmospheric pressure the rate of evaporation of water exposed to a wind of about 180 cm. per sec.$^{-1}$ was cut to about one-half by a film of cetyl alcohol, although the fatty acids produced no measurable effect.

It was pointed out that there are two factors that determine the rate of evaporation. There must be a drop in the partial pressure of the water vapor as it diffuses through the air overlying the liquid, but the effect of a film of cetyl alcohol is to offer a resistance to diffusion which resides in the monolayer itself.

Instead of dealing with the *rates of evaporation* of the water in g. cm.$^{-2}$ sec.$^{-1}$ there is thus an advantage in considering the *resistance to evaporation* which may be assumed to be proportional to the reciprocal of the rate measured in cm.^{2} sec. g^{-1}. The resistance to diffusion through the air overlying the water is not affected by the presence of a film. When, however, a film is present, there is also a resistance characteristic of the film itself which is in series with the air film resistance. Two experiments in succession—the first with a film on the water,

* This paper was read at the Symposium on Surface Chemistry held under the auspices of the American Association for the Advancement of Science at the University of Chicago, September 24, 1941. It will soon be published by the AAAS in a series of contributions on the subject of surface chemistry.

[1] E. K. Rideal, *Jour. Phys. Chem.*, **29**, 1585 (1925).

[2] I. Langmuir and D. B. Langmuir, *Jour. Phys. Chem.*, 31, 1719 (1927).

the second with a clean water surface—give data for the calculation of the characteristic resistance of the film which should be independent of such extraneous factors as the wind velocity and the pressure of the atmosphere. This resistance is simply the difference between the reciprocals of the rates in the two experiments.

An analysis of Rideal's data showed that at 25° C. a film of stearic acid offered a resistance of 300 units, while oleic acid gave a resistance of 850 units, but the experiments with cetyl alcohol gave a resistance of 60,000 units, roughly a hundred times greater than given by the fatty acids.

Sebba and Briscoe [3] have recently passed a stream of dry air inwards from the edge of a metal disk 0.3 cm. above the surface of water in a tray which is provided with barriers and a surface balance. By withdrawing air from a tube at the center of the disk at the rate of two liters per minute and measuring the water content of this air, they determined the relative rates of evaporation with and without films and with films exposed to different surface pressures F in dynes per cm. They found that films of oleic acid and cholesterol even when compressed did not cut down the rate of evaporation. Stearic acid had no effect up to $F = 20$, but then there was a rapid decrease until at $F = 40$ the rate of evaporation was only 36 per cent. of that from pure water. The aliphatic alcohol with 18 carbon atoms showed no effect up to 10 dynes, but at 30 dynes the rate fell to 42 per cent. Still greater effects were had with the alcohol having 20 carbon atoms. Here the evaporation was 92 per cent. at 5 dynes, 18 per cent. at 20, 12 per cent. at 40 and only 1 per cent. at $F = 48$.

They made no attempt to calculate resistances or express their data in quantitative units giving rates per unit area. Although their rates decreased as F was increased, and the length of hydrocarbon chain increased, they did not give any theory or analysis of these data.

In another paper, Sebba and Briscoe [4] found that the great decrease in rate produced by the C_{20} alcohol gradually disappeared in a few hours when the film was allowed to remain on the surface under only small pressure but that this effect

[3] F. Sebba and H. V. A. Briscoe, *Jour. Chem. Soc. (London)*, 106 (1940).
[4] F. Sebba and H. V. A. Briscoe, *Jour. Chem. Soc. (London)*, 128 (1940).

did not occur if the film was maintained under high pressure. They found in blank runs that no appreciable amount of impurity accumulated on the surface during a similar time when no alcohol film was present. As an explanation of this decrease in rate with time, they suggest, quite *ad hoc*, that a slow association of the alcohol molecules by adhesion between the hydrocarbon chains occurs, giving double molecules with an $-OH$ group at each end.

Our experience has generally been that slow effects of this kind are due to impurities. There are logical reasons for believing that a very small amount of an impurity which offers little resistance should have a very great effect in increasing the permeability of a film to water. Let us assume, for example, that we have a film of cetyl alcohol having a specific surface resistance of 60,000 units and we have another substance like oleic acid, with a specific resistance of 600 units. With a film made from a mixture of these substances we have to deal with resistances in parallel—not in series. We therefore should add the conductances to get the average conductance of the film. If we had only one per cent. of oleic acid in the film, its partial conductance would be about equal to that of the cetyl alcohol, so that about 1 per cent. of oleic acid would reduce the evaporation resistance to one-half.

It is evident therefore that amounts of impurity far too small for Sebba and Briscoe to have detected might easily account for the gradual increase in the rate of evaporation that they observed with the alcohol films.

We undertook experiments to test this hypothesis of the sensitivity of impermeable films to traces of permeable substances. We anticipated that the effect would be very much like that of minute conducting particles in an insulating film on a condenser plate giving a kind of short-circuiting effect. In the experiments that we planned we wished to retain the advantage of Sebba and Briscoe's experiments of measuring the rate of evaporation from an extended surface of water in a tray with films that could be subjected to pressure. Their experimental procedure, however, was time consuming and suffered from the disadvantage that it did not easily give quantitative data expressible as rates per $cm.^2$. In their

experiments the air moving radially inward became gradually more humid, so that all parts of the surface were not acting in parallel.

Experimental Method. Preliminary experiments showed that the rate of increase of weight of a drying agent such as calcium chloride supported on a wire gauze just above the surface of the water in a trough gave a very simple and reliable measurement of the rate of evaporation. This method has the advantage that there is uniform evaporation over a large surface.

The apparatus used is shown in Fig. 1, a tin ointment box was chosen having a tightly fitting cover, the box being 9.6

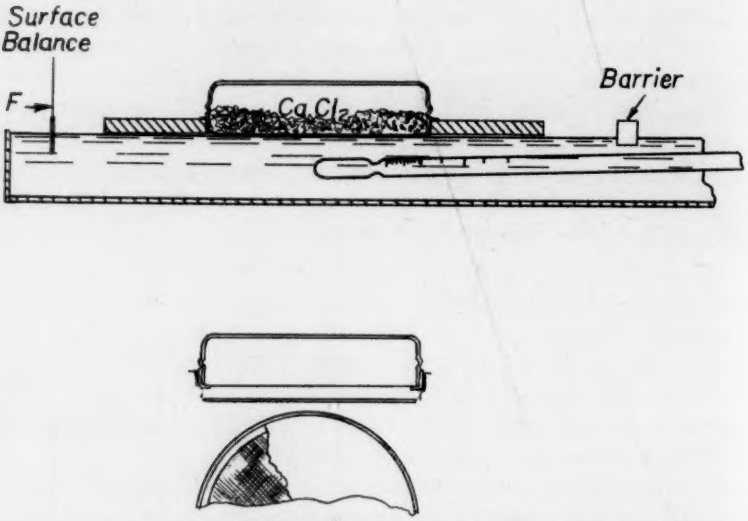

FIG. 1. The drying box and its arrangement over the water of a trough.

cm. in diameter and 2.2 cm. deep. A circular hole 8.9 cm. in diameter was cut out of the cover and across this opening was stretched a copper gauze (50 meshes per inch of wire 0.006 inches diameter). Another cover was spun to a slightly larger diameter so that it could be fitted tightly over the first cover that supported the gauze. The apparatus thus consisted of three parts, which could be separated from one another: the container, the gauze frame, and the cover. In

normal use the whole device was turned upside down as indicated in Fig. 1, the container being on top, the cover at the bottom.

With the parts in this position but separated, the gauze was covered with a uniform layer about 3 mm. thick of fine granular calcium chloride (about 50 grams) and this was immediately covered with the container and the cover was then applied under the gauze. The calcium chloride used has the composition $CaCl_2.2H_2O$.

The water surface from which the evaporation was to be measured was contained in a long trough, 20 cm. wide and 100 cm. long, shown in Fig. 1. This was provided with a surface balance to measure the spreading force F (dynes per cm.) and a barrier which could be used to scrape the surface or compress a monolayer which had been spread upon the water. The trough was levelled by means of a spirit level and the depth of the water in the trough was kept constant to within less than 0.1 mm. by a submerged hydrophilic point of glass which just touched the surface. As the water evaporated more was added from time to time, bringing the surface just to the tip of this point.

A heavy square brass plate 25 cm. square and 6 mm. thick was provided with a large circular hole, 9.7 cm. diameter, into which the drying box could be inserted. A flange on the gauze frame of the drying box was located so that when the box was inserted in the hole the lower surface of the wire gauze was flush with the lower surface of the brass plate. A series of brass tubes (not shown in Fig. 1) were made all having an inside diameter of 8.9 cm. but having various lengths. These were arranged so that any one of them could be fitted into the hole in the brass plate so as to support the drying box at various heights above the water surface. The heights chosen were 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 2.0, 4.0 and 6.5 cm. The brass plate was supported over the trough so that its lower surface was always 0.2 cm. above the water surface.

In a typical experiment for the measurements of the rates of evaporation the drying box containing the calcium chloride was weighed, the lower cover was quickly removed and the box was fitted into the hole in the brass plate or into one of

the brass tubes so that the gauze frame was at a known distance, b, above the surface of the water. The box was left in this position for a definite time interval measured by a stop watch, times of 2, 5 or 10 minutes usually being selected. At the end of the time interval the box was quickly lifted from the brass plate, the cover applied and the box was again weighed.

Using a surface of clean water which had been repeatedly scraped by moving barriers, experiments were made measuring the rate of evaporation in g. cm.$^{-2}$ sec^{-1}. At 25° C. and with a distance of 0.2 cm., the increase in weight was about 63 mg. per minute. Some blank runs were also made in which the brass plate, instead of being over water, was laid on a glass plate, all operations being conducted as in the usual experiment. The gain in weight under these conditions, which did not exceed one milligram, was used as a correction in the experiments.

In studying the effect of compressed monolayers measurements of the rate of evaporation were first made with a clean water surface and then with a surface covered by the monolayer. At the end of such a series the rate of evaporation from a pure water surface was again made, so as to detect any changes in the absorbing quality of the calcium chloride. It was found that there was only a very slow and steady decrease in the rate of taking up water vapor. During a long series of runs in which a total of about 1.5 grams of water was absorbed the rate of absorption of water (with $b = 0.2$ cm.) decreased from 62 mg. per minute to 58 mg. per minute.

From the rates of evaporation with and without the film the resistance to evaporation was calculated in accordance with the theory which will be described later. A check on the theory was obtained by varying the distance b between the water surface and the wire gauze supporting the calcium chloride. This naturally changed the actual rates of evaporation but it did not alter the resistance of the film.

The evaporation caused a perceptible cooling of the water surface. A thermometer was placed in the water about 5 mm. below the surface as shown in Fig. 1. During a five minute interval the temperature decreased as the result of evaporation by about 0.7° C. A cylindrical metal box filled with mercury

and of a diameter equal to that of the hole in the brass plate, was lowered into actual contact with the water surface. To produce a lowering of 0.7° in the same time in the thermometer reading it was necessary to cool the mercury by about 1.1°. We assume, therefore, that during the evaporation the lowering of the temperature of the surface of the water was about $1\frac{1}{2}$ times that shown by the thermometer. As this cooling effect was proportional to the rate of evaporation of the water it was affected by the presence of films and by alteration of the distance b.

The cooling of the water surface produced by the evaporation naturally decreased the vapor pressure of the water and caused the observed rates of evaporation to be lower than they would otherwise be. However, since there is only a small lowering of temperature the depression of the vapor pressure varied in proportion to the rate of evaporation. The effect was thus equivalent to that of an increase Δb in the distance between the water and the calcium chloride, and this increment would not be changed by the presence of a monolayer on the water surface. Thus the resistance of the monolayer, as calculated from the rates of evaporation with and without the monolayer, is not modified by the cooling effect.

Just as the evaporation of water from the trough cools the surface so the absorption of the water by the calcium chloride produces an appreciable rise in temperature. This temperature gradient, warm on top and cooler below, has a marked effect in preventing convection currents, and so gives a linear distribution of partial pressure of water vapor in accord with the ordinary laws of diffusion.

Let M be the mass of water (in g.), taken up by the calcium chloride in the time t (in seconds); A the cross sectional area of the diffusion tube (62.2 cm.^{2}); b the length of the diffusion path (in cm.), and D the diffusion coefficient of water vapor in air (in cm.^{2} per sec.). Then diffusion theory gives:

$$M/At = D(w - w_0)/b, \qquad (1)$$

where w is the concentration of the water vapor measured in g. per cm.^{3} at the surface of the water just above the monolayer, and w_0 is the concentration in similar units at the lower surface of the wire gauze.

Since the surface of the calcium chloride, with a rapid diffusion of water to it, becomes covered with a hydrate, the value w_0 is presumably not 0. It becomes important, to know whether it is reasonably constant. Since there may be appreciable resistance to the passage of the water vapor through the meshes of the copper gauze and into the lower layers of the calcium chloride it is desirable to replace Eq. 1 by the following:

$$M/At = D(w - w_0)/(b - b_0), \qquad (2)$$

where b is the distance from the lower surface of the gauze to the water and b_0 is the distance from the same point to the effective absorbing area of the calcium chloride.

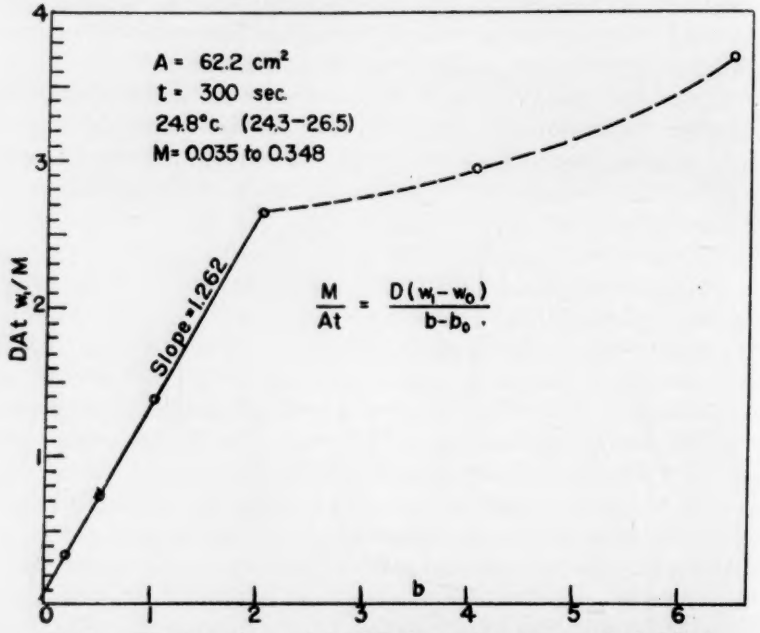

FIG. 2. The dependence of the diffusion resistance upon the height b of the drying box above the surface.

A series of measurements were made of the rate of evaporation of water as a function of the distance b, this being varied from 0.2 to 6.5 cm. The results are shown in Fig. 2 where the ordinates represent $DAtw/M$ and the abscissas represent b

measured in cm. The temperature of the water, as given by the thermometer in the position shown in Fig. 1, was recorded at the beginning and end of each evaporation run. From the mean temperature during the run the value of w was calculated from the data of the Smithsonian tables ($w = 17.12 \times 10^{-6}$ g. cm.^{3} at 20° C. and 22.78×10^{-6} at 25° C.). To eliminate effects resulting from changes in temperature due to cooling it was better to plot $DAtw/M$ rather than At/M.

Examination of Fig. 2 shows that for values of b up to 2 cm. the points lie accurately on a straight line whose slope according to Eq. 2 is equal to $w/(w - w_0)$.

The diffusion coefficient of water vapor in air (International Critical Tables, Vol. 5, page 62) is given by:

$$\log_{10} D = 1.75 \log_{10} T - 4.921. \qquad (3)$$

Thus at 20° C., $D = 0.249$ cm.^{2} sec.$^{-1}$ and at 25° C. it is 0.2563. We have made several direct measurements of the diffusion coefficient of water vapor and have satisfactorily checked the foregoing values.

The slope of the line in Eq. 2, 1.262, thus gives

$$(w - w_0)/w = 0.79, \qquad (4)$$

which corresponds to a relative humidity w_0/w at the surface of the calcium chloride of 21 per cent.

The intercept of the straight line in Fig. 2 on the b axis gives $b_0 = -0.07$ cm. Thus the distance measured from the lower surface of the wire gauze to the effective absorbing area is only 0.7 mm.

The fact that the line in Fig. 2 is straight proves that the partial vapor pressure of water at the effective absorbing surface is constant and corresponds to a relative humidity of 0.21. The equilibrium between $CaCl_2.2H_2O$ and $CaCl_2.4H_2O$ corresponds to a relative humidity of 0.144 (International Critical Tables, Vol. 7, page 294) at 25° C. For the equilibrium between hydrates containing 4 and 6 molecules of water the relative humidity at 25° C. varies from 0.18 to 0.22 depending whether the α or β form of the hydrate is present. It thus appears that under the conditions of our experiment, with a rapid supply of water vapor, the hydrate containing 6 molecules is formed, but no liquid phase is pro-

duced. The calcium chloride after having absorbed 1 or 2 g. of water vapor showed no tendency to cake together as it would if any liquid phase had been produced.

Figure 2 shows that when b was greater than 2 cm. the reciprocal of the evaporation rate no longer increases linearly. This effect is obviously due to convection, resulting from minute temperature differences. It has been shown [5] that close to a heated surface in open air there is a film of relatively stationary air of several mm. thickness through which diffusion and heat conduction must occur.

The actual rate of evaporation given by the data of Fig. 2 with $b = 4$ cm. corresponds to diffusion through a layer of quiet air of 2.3 cm. thickness while with $b = 6.5$ cm. the equivalent layer is 2.9 cm. The thermal stratification of the air over the water surface thus gives a very high degree of stability and prevents convection up to values of b as great as 2 cm.

Evaporation Resistance of Monolayers. The reciprocal of the rate of evaporation is not a wholly satisfactory measure of the rate of evaporation. For example, it does not take into account the effect of the variation of vapor pressure resulting from changes of temperature. By analogy with Ohm's law, $C = V/R$, it is desirable to define the evaporation resistance by an equation of the type: Rate = Driving Force/Resistance. Let us consider the resistance offered by the layer of air of thickness b in the experiments represented by Fig. 2. The greater the vapor pressure of the water (produced by raising the temperature), the greater will be the rate of evaporation with any given value of b. This increase in pressure is analogous to an increase in the voltage of an electric circuit. The flow of water vapor M/t corresponds to the electric current. We might measure the driving force by the difference of the partial pressures, $p - p_0$. It is however better to use $w - w_0$ which varies in proportion to $p - p_0$, because by so doing we employ the same units of mass that are involved in M/t. The logical analog of Ohm's law thus becomes

$$M/t = (w - w_0)/\Omega, \qquad (5)$$

[5] I. Langmuir, *Phys. Rev.*, **34**, 401 (1912); ibid., **12**, 368 (1918); *Trans. Amer. Electrochem. Soc.*, **23**, 299 (1913).

where Ω is defined as the evaporation resistance. By comparing Eqs. (5) and (2) we see that the resistance of the air column for the experiment of Fig. 2 is:

$$\Omega = (b - b_0)/AD. \tag{6}$$

In our studies of the resistances of monolayers we are interested in knowing the specific surface resistance, that is the resistance that would correspond to a unit of area. Since by Eq. (6) Ω varies in inverse proportion to the area A we may define the specific surface resistance by:

$$\omega = A\Omega. \tag{7}$$

Comparing this with Eq. (5) we find that ω can be calculated from the observed rates of evaporation by the equation

$$\omega = (Atw/M)(w - w_0)/w. \tag{8}$$

When we use $CaCl_2.2H_2O$ in the drying box the value of $(w - w_0)/w$ in accord with Eq. (4) is 0.79. We may insert this value in Eq. (8). Furthermore we recognize that ω represents two resistances in series: ω_b is the resistance of the air layer of thickness $b - b_0$ and ω_f is the resistance of the surface itself including that of a monolayer. Eq. (8) thus becomes:

$$\omega = 0.79Atw/M = \omega_b + \omega_f, \tag{9}$$

where

$$\omega_b = (b - b_0)/D. \tag{10}$$

By defining surface resistance in this way the equations have been much simplified and the value of ω does not depend upon the units of mass or of pressure as it would if we had taken $p - p_0$ as the analog of voltage. The specific resistance ω has the same dimensions as the reciprocal of a velocity, that is it is measured in seconds per cm.

Because of the finite velocity with which molecules leave the surface of an evaporating liquid there is a definite limiting surface resistance, ω_0, even for a water surface which has no monolayer on it.

Let us consider a surface of water covered by a monolayer and let this be in thermal equilibrium with its own vapor. The molecules in the vapor are moving in random directions

at an average velocity given by

$$v = (8RT/\pi M_c)^{1/2}, \tag{11}$$

where M_c is the (chemical) molecular weight, and $R = 8.32 \times 10^7$ ergs deg^{-1}.

The rate at which molecules impinge on the surface, in g. cm.$^{-2}$ sec.$^{-1}$, is given by

$$M/At = wv/4. \tag{12}$$

Of these molecules which strike the surface we will assume that a fraction α condense and enter the liquid phase. We may call α the condensation coefficient. The fraction $1 - \alpha$ of the molecules act as though they are reflected from the surface. Actually, however, they condense on top of the monolayer but are held by such small forces that they evaporate so rapidly that no appreciable number are present at any given time in this adsorbed layer.[6]

Under equilibrium conditions the rate at which the molecules condense is therefore $\alpha wv/4$, and the rate at which they evaporate must be equal. Since the evaporation and the condensation phenomena are independent of one another the rate of evaporation will not be modified by changing the vapor pressure above the liquid, so the true rate of evaporation into a vacuum is given by:

$$M/At = \alpha w(RT/2\pi M_c)^{1/2}. \tag{13}$$

The surface resistance corresponding to this rate of evaporation can be obtained from Eq. (8) by putting $w_0 = 0$, giving

$$M/At = w/\omega_f, \tag{14}$$

where w is the equilibrium vapor density, which is not altered by the presence of a monolayer.

Combining Eqs. (14) and (13) we find

$$\omega_f = (1/\alpha)(2\pi M_c/RT)^{1/2} = (2.75 \times 10^{-4}/\alpha)(M/T)^{1/2}. \tag{15}$$

For water at 20° C. ($M = 18$, $T = 293$) this gives

$$\omega_f = 6.8 \times 10^{-5}/\alpha \text{ sec./cm.} \tag{16}$$

[6] I. Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 141 (1917).

Comparison of Eqs. (15) and (11) shows that

$$1/\omega_f = \alpha v/4. \tag{17}$$

Thus the value of ω_0 for a clean water surface for which $\alpha = 1$ is the reciprocal of one-fourth of the average molecular velocity.

If we make an experimental determination of ω_f the resistance due to a film spread upon the water we can calculate the condensation coefficient α for this film, by Eq. (16)

$$\alpha = 6.8 \times 10^{-5}/\omega_f. \tag{18}$$

Langmuir and Langmuir [2] took the evaporation resistance of a film to be the change in the value of At/M produced by the film. When we compare this with Eq. (8) we see that we can express the old data for film resistance in terms of our new units by multiplying the old values by $w - w_0$. From Rideal's data at 25° C. we thus calculate that for an oleic acid monolayer (presumably at $F = 29$ dynes/cm.) $\omega = 0.019$ sec. cm.$^{-1}$, while for stearic acid (at an unspecified but presumably low value of F) $\omega = 0.007$ sec. cm.$^{-1}$. The data presented by L. and L. for cetyl alcohol monolayers were obtained by measuring the rate of evaporation into air of an unspecified humidity. If we assume that the relative humidity was 50 per cent. then for these films $\omega = 0.6$ sec. cm.$^{-1}$. From these data by Eq. (18) we find that the condensation coefficients α are; for oleic acid 0.0036, for stearic acid 0.0010 and for cetyl alcohol 0.00011. Thus the true rate of escape of molecules from the surface was decreased in the ratio of about 10,000 to 1 by the presence of a cetyl alcohol monolayer.

An Energy Barrier as a Cause of Evaporation Resistance. There are two conceivable mechanisms which could account for low values of α. It might be that the resistance ω_f is essentially due to slow diffusion of water through the monolayer. A second possible factor would be an energy barrier that opposes the penetration of water molecules into the film or some part of the film.

A diffusion resistance would increase in proportion to the thickness of the film. Similarly if there are a number of energy barriers in series the total barrier resistance that results from them is the sum of the separate resistances.

The concentration of molecules in any region is decreased in a ratio n/n_0 at an energy barrier of magnitude λ, where λ represents the energy per molecule needed to bring the molecule to the height of the barrier. The Boltzmann equation gives for n/n_0

$$n/n_0 = \text{exp. } (-\lambda/kT). \tag{19}$$

Apart from a numerical coefficient which depends upon geometrical factors and steric hindrance, but is probably of little significance in the present case, the value of the condensation coefficient will be given by

$$\alpha = \text{exp. } (-\lambda/kT). \tag{20}$$

If the height of an energy barrier is doubled it does not double the value of α but it gives a new value of α equal to the square of the old value.

It was pointed out in 1927 [2] that the very small values of α produced by cetyl alcohol could not reasonably be explained as a diffusion resistance for it would require that the concentration of water within the film should be of the order of 10^{-8} g. cm.$^{-3}$, very much less than any observed solubility of water in oil. A test of this hypothesis of diffusion resistance can be made by considering the effect of varying the thickness of the film.

It was pointed out also that when a water molecule penetrates the monolayer it must push the other molecules apart and so produce a momentary increase in area which may be represented by a_0. If the film is under a surface pressure F there is thus an energy barrier Fa_0 which must be overcome. Taking $a_0 = 8\,A^2$ and $F = 30$ dynes cm.$^{-1}$ we find that the energy barrier is $\lambda = 2.4 \times 10^{-14}$ erg, which corresponds to 360 cals. per g. mole. Putting $T = 300°$ we then find by Eq. (20) $\alpha = 0.55$. Thus the barrier corresponding to the energy necessary for a molecule of water to penetrate into a monolayer under a pressure of 30 dynes cm.$^{-1}$ could account only for a reduction in α from 1 to 0.55. To give a value of α as low as 0.0001 would require an energy barrier of 3.7×10^{-13} erg or 5500 cals. per g. mole., about 16 times as great as that which would correspond to a water molecule forced into a film at 30 dynes cm^{-1}.

There is another useful way of considering the problem. If a monolayer of a thickness of 24 A (a condensed film of stearic acid) is under a pressure of $F = 30$, the average pressure in the film is about 125 atmospheres. Let this pressure be represented by P and let v_0 be the volume of the water molecule (about 30 A^3), then the energy barrier corresponding to molecules subjected to this pressure would be $\lambda = Pv_0$. To account for the value $\alpha = 0.0001$ the pressure P would have to be 12,000 atmospheres which would require a surface pressure of 3000 dynes cm.$^{-1}$ *if the pressure were uniformly distributed through the thickness of the film.*

We thus conclude that the observed high evaporation resistances of some films involve forces upon single molecules of water of the order of 100 times greater than those previously known to exist in monolayers. Sebba and Briscoe have proved that the evaporation resistance of films increases rapidly when the pressure is raised. This increase is far greater than could be accounted for directly by a barrier Fv_0.

Experimental Determination of Evaporation Resistances of Monolayers of Pure Substances. Our experiments with the drying box which has been described were made for the purpose of throwing light upon these rather puzzling theoretical questions. We wished particularly to find whether ω_f varies in proportion to the thickness of the film as it would by the diffusion hypothesis or whether log ω_f varies linearly with F and with thickness of the film. We have made a large number of experiments with the highly purified fatty acids having 16, 18, 19, 20, 21, and 23 carbons. These will be represented in general by the symbol C_{18}, C_{23}, etc. We have also studied the C_{20} aliphatic alcohol. Many experiments were made to determine the effect of the pH of the substrate and of the presence of barium and cadmium salts.

In most experiments the force F was increased in a series of steps and the position of the barrier was noted in each case so that the force-area curve of the compressibility of the film could be determined. In our later experiments care was taken to make sure that all of the applied substance was completely spread as a monolayer but in some of the earlier experiments where such precautions were not taken, the areas per molecule,

although correct as regards relative value may be too low in absolute magnitude.

The fatty acids C_{19}, C_{21}, and C_{23} were purchased from F. Francis and were the preparations of exceptionally high purity that were used for the determinations of freezing points and other properties reported by Francis, Collins and Piper.[7] The C_{20} alcohol was a very pure product given to us by Dr. E. Emmet Reid. The stearic acid, C_{18}, and arachidic acid, C_{20}, were prepared for us in this laboratory by Dr. R. E. Burnett by fractionation of esters. The sample of stearic acid is very pure but we know that the C_{20} contained small amounts of neighboring acids.

Weighed amounts of the acids or alcohol were dissolved in benzene and weighed amounts of these solutions were placed upon the water surface by means of a pipette. Precautions were taken to avoid errors due to changes in concentration of the solutions by evaporation.

When drops of a dilute solution of benzene and a fatty acid are placed on a clean water surface they move about vigorously over the surface. It is very important that they should not come into contact with the edges of the trough. We have found a simple means of localizing the spreading action within a definite region near the center of the trough. A shallow glass dish with a thick hydrophilic rim is placed under the surface of the water in the trough. For this purpose we have used the glass cover of a staining jar of the type known as the Coplin jar. The edge of the cover which rests on the jar has a plane ground glass surface which renders it hydrophilic. Inverting the cover so that the rim turns up like a saucer, we have ground the bottom of the dish so that it also has a plane surface. The dish has an outside diameter of 6.0 cm. and an inside diameter of 5.0 cm. The dish is supported on glass plates in the center of the trough so that the ground upper surface of the rim lies about 1 mm. below the surface of the water in the trough.

When drops of benzene containing a fatty acid are placed upon the water over the center of the submerged dish they move around only within the limits of the dish. The mono-

[7] F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. London*, **158A**, 691 (1937).

layer which flows radially out from the drops exerts a viscous drag on a thin layer of underlying water and thus lowers the level of the water within the dish, until the out-flow is balanced by a gravity in-flow close to the rim of the dish. The amount of depression thus depends upon the width of the edge and its depth below the water surface. The drops of the benzene solution always stay within this depressed portion of the surface.

When this method of spreading is not used the drops are apt to break into many droplets some of which evaporate leaving minute crystals of fatty acid which do not spread. With the submerged dish the spreading is under much better control and if, as rarely happens under these conditions, any residual crystals remain on the surface they can be readily seen because one knows where to look for them.

The arrangement of the trough, the drying box, surface balance and barrier were not exactly as shown in Fig. 1. The trough was 100 cm. long and 20 cm. wide. The surface balance marked *F* in Fig. 1 was 15 cm. from one end. The edge of the brass plate which supported the drying box was about 1.5 cm. from the surface balance. The water surface was first cleaned by repeated motions of the barrier from the edge of the brass tray to the far end of the tray. Any contamination of the surface under the brass plate was removed by blowing air from the surface balance under the brass plate. Immediately after cleaning the water surface a glass plate was placed about 5 mm. over the water so as to protect all parts of the water surface from contamination by dust.

At the beginning of each series of measurements of evaporation resistance the drying box was weighed and was then inserted into the hole in the brass plate for two minutes. The increase in weight was used to calculate ω_b by Eq. (10).

The weighed amount of benzene solution of the spreadable substance was then applied to the water surface over the submerged dish through a small hole in the glass plate and the hole was then covered. By thus spreading the film from the center of the trough any traces of impurities on the surface were driven to the two ends of the trough. The film under the drying box had thus never been exposed to contamination by dust. When the spreading of the film was complete and

careful examination had shown no residual crystals of fatty acid over the dish, the barrier was removed to exert a pressure on the monolayer, indicated by the surface balance. The position of the balance barrier F in Fig. 1 was always kept constant within about 0.1 mm., and the distance from F to the movable barrier at the other end of the trough was also measured within 0.2 mm. From these data the area per molecule, a, was calculated.

In general, the surface pressures F were raised in definite steps of 2, 3, or 5 dynes cm.$^{-1}$. At certain selected values of F (usually multiples of 5), the drying box was applied and the increase in weight in a 2, 5, or 10 minute interval was determined. When the drying box was removed it was always replaced by a cover.

From the increase in weight the value of ω was calculated by Eq. (9). In a series of measurements with a given monolayer the pressure was often raised to a high value and then lowered again and in some cases several such cycles were completed. At the end of the series the monolayer was scraped off by using several barriers in succession and all trace of remaining film was blown out from under the brass plate. Another determination of ω_b was then made with a clean water surface. Linear interpolation between the initial and final values of ω_b was used to allow for the progressive slight change in ω_b during the successive measurements. The values of ω_f were then obtained by subtracting ω_b from ω.

Figure 3 gives typical data for ω_f obtained with monolayers of the C_{18}, C_{20}, and C_{23} acids spread upon water acidified with H_2SO_4 pH 3. The lowest curve marked by crosses was obtained with the C_{20} acid spread upon water which had been twice distilled, the second distillation being from a quartz condenser. The CO_2 from the air gives the pH 5.8.

It is evident from these data that log ω_f is approximately a linear function of F, and the slopes of the lines are approximately equal. An increase in length of the hydrocarbon chain causes a marked rise in log ω_f. Since log ω_f measures the height of the energy barrier we should expect a linear dependence of log ω_f upon n the number of carbon atoms in

the acid. The coefficients in the equation

$$\log_{10} \omega_f = -3.08 + 0.0425F + 0.122n, \qquad (21)$$

which expresses these linear relationships, have been chosen to fit the data of Fig. 3. The three parallel dashed lines near

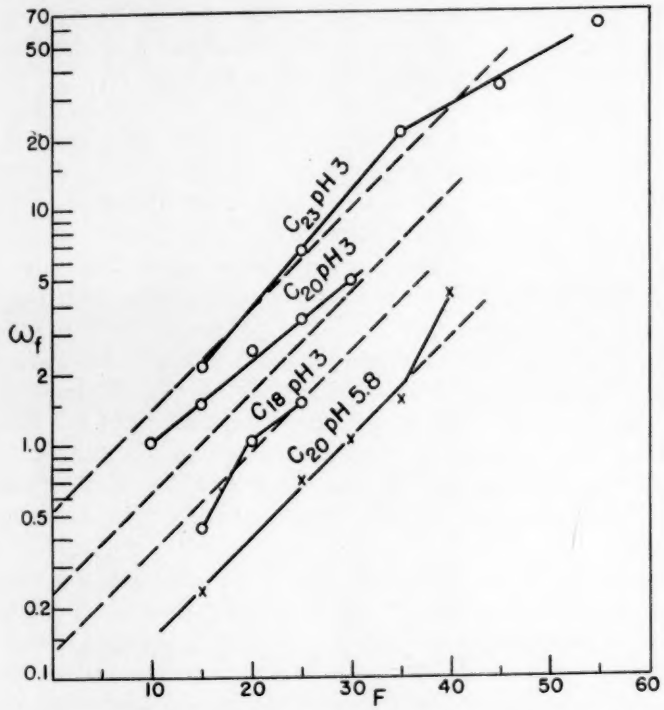

FIG. 3. The evaporation resistance for monolayers of the C_{18}, C_{20}, and C_{23} acids on dilute H_2SO_4pH 3, and the C_{20} acid on distilled pH 5.8.

the upper three curves are plots of this equation for $n = 18$, 20 and 23.

Although the agreement is not very close, the equation gives a useful approximation to the observed values. We shall see that traces of impurities and slight uncontrolled differences in experimental technique may cause variations comparable to the deviations of the calculated lines from the experimental data.

The curve for the C_{20} acid on distilled water is very much lower than the curve for this acid on pH 3 water. Other less accurate data with other acids have given general confirmation of this conclusion, that the values of ω_f obtained at pH 3 are always much higher than those found on distilled water. The line for the C_{20} acid on water of pH 5.8 is approximately parallel to the others and can be represented by Eq. (21) if we change the term -3.08 to -3.70. The lowest of the dashed lines represents this modified equation for $n = 20$.

Towards the end of our experiments on evaporation resistances (Sept. 1940) two experiments were performed with more strongly acidified water, dilute H_2SO_4 pH 2. With the C_{20} acid values were obtained which were about one-eighth those previously obtained with the dilute H_2SO_4 of pH 3. The semilog plot of ω_f gave a line a little below that shown in Fig. 3 for C_{20} pH 5.8. Another run was made with the C_{23} acid and dilute H_2SO_4 pH 2. This gave a series of points on the semilog plot which formed a good straight line, parallel to the theoretical dashed lines of Fig. 3 with values of ω_f about one-seventh as great as those obtained at pH 3. Unfortunately the experiments were discontinued about this time. The results suggest that the maximum values of ω_f occur at some definite value of pH that probably lies between 3 and 5.8.

The value $\omega_f = 62$ sec. cm.$^{-1}$ for the C_{23} acid on pH 3 water at $F = 55$ is the highest evaporation resistance which we have found. The value of ω_b with $b = 0.2$ cm. averaged about 1.1 sec. cm.$^{-1}$. Thus the rate of evaporation was cut down to 1/50 by the presence of this monolayer at this value of F. Sebba and Briscoe have reported a single observation in which the evaporation rate was cut to 1/100 by a monolayer. This was found with the C_{22} alcohol at $F = 48$ although at $F = 40$ this alcohol gave a rate 0.12 of that from water. Roughly these points would correspond to $\omega_f = 120$ at $F = 48$ and 10 at 40.

$F(a)$ Curves. Figure 4 shows typical curves that we have obtained by plotting F in dynes cm.$^{-1}$ as a function of a, the area per molecule expressed in sq. A units. These $F(a)$ curves for fatty acids on water of pH less than 7 and for the higher alcohols consist in general of two straight lines such

as AB and BC in Fig. 4. The intercept of the extension of the line CB on the a-axis we shall designate by D.

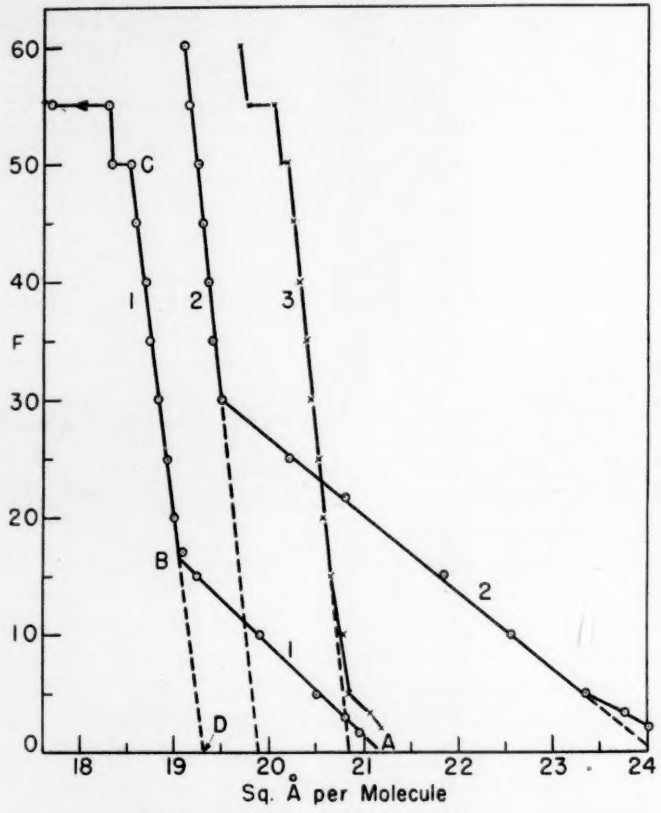

FIG. 4. Typical $F(a)$ curves for condensed water films.

Curve 1—C_{20} alcohol on distilled water.

Curve 2—C_{23} acid on dilute H_2SO_4 pH 3.

Curve 3—Ba salt of C_{20} acid on 10^{-4}M $BaCl_2$ adjusted to pH 7.0 with $KHCO_3$.

Tables I, II, and III summarize our observations on the $F(a)$ curves for the films we have studied. The figures given in parenthesis are data given by Nutting and Harkins.[8]

With the fatty acids on water at pH 3 the areas at the points A and D decrease only very slightly as n increases.

[8] G. C. Nutting and W. D. Harkins, *Jour. Amer. Chem. Soc.*, **61**, 1180 (1939).

The value of F_B increases by about 1 dyne cm.$^{-1}$ for each additional carbon atom.

In the Tables I, II, and III the fifth column gives F_C, the pressure at which collapse occurs. The increments of pressure

TABLE I.

Fatty Acid Films on Dilute Sulfuric Acid pH 3.

	a_A.	a_D.	F_B.	F_C.	$-da/dF$ AB.	$-da/dF$ BC.
C_{16}		(26.75)		(22.51)		
C_{17}		(24.59)		(27)	(0.180)	
C_{18}	25.0 (24.11)	20.4	24	30 (21)	0.202 (0.178)	0.0130
C_{19}	(24.0)		25	>50 (29)	0.165 (0.163)	0.0115
C_{20}	24.7 (23.6)	20.4	27	32 (28.5)	0.174 (0.159)	<0.019
C_{21}			27	>45	0.17	0.011
C_{23}	24.6	20.2	30	>60	0.158	0.016
C_{20} Alcohol	21.8	19.8	17	50	0.134	0.0120

TABLE II.

Fatty Acid Films on Distilled Water pH 5.8.

n.	a_A.	a_D.	F_B.	F_C.	$-da/dF$ AB.	$-da/dF$ BC.
20	24.5	21.4	26.0	40	0.16	0.015
21	23.5	19.7	28.4	>50	0.144	0.0115
23	22.2?	18.2?	28.0	>60	0.140	0.008

were usually 2 or 3 dynes cm.$^{-1}$, although at pressures above 50 these increments were often 5 dynes cm.$^{-1}$. Thus when it is stated in the table that collapse was observed at 32 dynes cm.$^{-1}$ for a C_{20} acid this means that no appreciable changes in area occurred at 30 dynes cm.$^{-1}$ during the four minute period during which measurements of evaporation resistance were being made, but that an appreciable rate of decrease, such as

TABLE III.

Films of Fatty Acids on 10^{-4} $BaCl_2$ Adjusted to pH 7 by $KHCO_3$ ($2 \times 10^{-4}M$).

n.	a_A.	a_D.	F_B.	F_C.	$-da/dF_{AB}$.
C_{14}				5	
C_{16}				<30	
C_{18}				45 †	
C_{19}				60	
C_{20}	21.3	20.9	5	50 *	0.015
C_{21}				>60	
C_{23}	21.2	19.6	10	>60	0.026

* The pH in this case was 9.0. There was a limited decrease in area at $F = 30$.

† Very slow temporary collapse observed even as low as 5 dynes.

0.2 per cent. per minute, was observed at $F = 32$. The notation $F_C > 50$ for the C_{19} acid means that at 50 dynes no change in area was observed but an appreciable decrease in area did occur at the next higher reading, which in this case was 55 dynes cm.$^{-1}$.

With the acids and the C_{20} alcohol on water at pH 3 and pH 5.8 the collapse point was very definite. For example, with the C_{23} acid at $F = 60$ no change in area as great as 0.1 per cent. occurred during four minutes but at $F = 62$ there was a progressive change of about 0.5 per cent. per minute. In the case of the C_{20} alcohol as shown in curve 1 of Fig. 4 there was a decrease of about 1 per cent. in four minutes at $F = 50$ and about 4 per cent. in four minutes at $F = 55$.

With the films spread on 10^{-4}M. $BaCl_2$, at pH 7 the collapse point as shown by curve 3, Fig. 4, was not at all definite. A slow change in area of 0.2 per cent. in four minutes was often observed at pressures as low as $F = 20$ or 25. At $F = 50$ the change in four minutes would often be 0.5 per cent. At still higher pressures collapse became much more rapid but sometimes after having started seemed to reach a limiting value. On the other hand with the barium salt of the C_{18} acid at pH 7 a limited collapse of this kind at $F_C = 45$ was followed by subsequent decreases in area at

pressures as low as $F = 10$. This peculiar property of the barium stearate films is probably one of the factors that makes it so easy to build up monolayers from them. Multilayers of the pure fatty acids can be built only with great difficulty.

The data for F_c shown in parentheses in Table I are the highest values at which Nutting and Harkins were able to measure the film areas of fatty acids. They state that at pressures above these collapses set in, but the collapse pressures were not accurately reproducible. Their values of F_c are surprisingly low compared to those which we have found. Thus their measurements did not extend to sufficiently high values of F to enable them to observe the kink at B, which is shown with great distinctness in all of our data. For example, we found no collapse of the C_{19} acid at $F = 50$ whereas Nutting and Harkins found collapse at $F = 29$.

Of course, we do not definitely know why Nutting and Harkins were unable to use higher pressures for fatty acids, but some of our experience suggests a probable reason. In spreading films for building up multilayers it is necessary to keep the films on the water surface for long periods of time, and as the film is used up new films must be spread on the surface. In spite of great care in obtaining the best grade of distilled water (even using a quartz condenser in the last distillation), we have usually found that the first films have distinctly different properties from those that are subsequently spread upon the same water. With films containing barium or cadmium this difference often shows up in the higher rigidity of the first film making it difficult to deposit satisfactory multilayers. After the second or third applications of monolayers to the surface constant and reproducible results are obtained.

In some of our early experiments with fatty acids on quartz distilled water, pH 5.8, we found that F_c was very much lower for the first film than for the second or third films spread on the same water. For example, with the C_{18} acid it was sometimes found that the film collapsed at a rate of as much as 10 per cent. per minute with $F = 17$. In other cases this collapse rate might first be observed at $F = 25$. The immediate replacement of the film by a new one did not have much effect in increasing F_c. If the monolayer was left on the surface

for twenty minutes or more and then replaced there would be a large increase in F_c but sometimes it was necessary to apply a third film before a definite reproducible value of F_c was reached. As a result of this experience it was our common practice each day to put new water in the trough and to apply one or two fatty acid films during the first half hour before beginning a regular series of measurements.

These observations point strongly to the presence of minute traces of impurities which cause easy collapse of the film. These impurities are apparently removed by adsorption by the monolayer. We have previously reported similar studies of the removal of minute traces of Al ions from water by stearic acid films.[9]

It is an interesting fact that the values of F_c are much higher for the acids which have an odd number of carbon atoms. Thus F_c for the C_{19} acid exceeds by 19 units the average for the C_{18} and C_{20} acids and the value for the C_{21} acid is 13 units higher than that for the C_{20}. Nutting and Harkins' data confirm this conclusion. Their value for the C_{19} acid exceeds by 5 units the average of the C_{18} and C_{20} acids, and their value for the C_{17} acid is about 5 units higher than the average of the C_{16} and C_{18}. Since it is known that the alternation in the properties of the fatty acids is limited to the crystalline state this fact is a strong indication that the condensed films of these substances under high pressure approximate closely to crystals. It is thus probable that each hydrocarbon chain which when extended has a zigzag arrangement of carbon atoms, is in step with its neighbors.

Whenever the pressure was raised so high that a collapse of more than 1 or 2 per cent. occurred the evaporation resistance of the film was very greatly decreased, often to one-tenth of its former value.

When the collapse occurs in the films we have studied the whole surface of the monolayer becomes covered with very fine lines that can be seen by dark field illumination. In other cases there are very fine starlike points of light. The uniformity of such a structure is a good indication of the purity of the film and of the care with which it has been spread. With some of the films when an attempt was made to raise the

[9] I. Langmuir and V. J. Schaefer, *Jour. Amer. Chem. Soc.*, **59**, 2400 (1937).

pressure above $F = 60$ it was found that collapse occurred only close to the barrier which was moved and that the film was so rigid that no additional force could be transmitted through the film to the surface balance. This phenomenon was never observed in our experiments at lower values of F. We believe, therefore, that the whole film was under a uniform surface pressure.

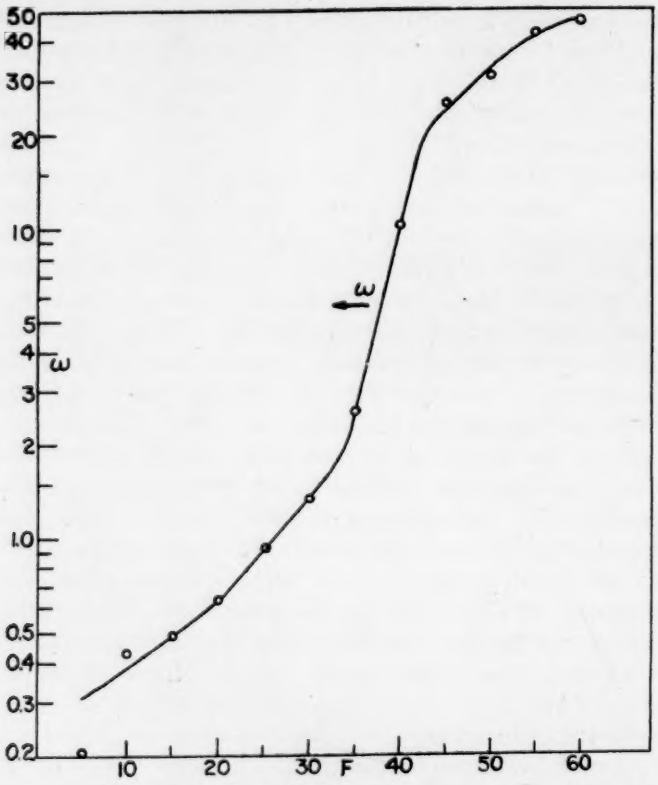

FIG. 5. Evaporation resistance for a monolayer of the C_{23} acid on distilled water pH 5.8.

Figure 5 gives values of evaporation resistance for the C_{23} acid on distilled water. It is seen that at the highest pressures the values of ω_f are not greatly different from those observed on acidified water (Fig. 3.) but at $F < 30$ the values are about

one-eighth as great. Between $F = 35$ and $F = 40$ there is an extremely rapid rise in ω_f. With the fatty acids C_{19} and C_{20} on distilled water this steep part was not apparent. A broken curve of this kind for the semilog plot of ω_f is also shown in the curve for the C_{18} acid on 10^{-4}M. Ba at pH 7 in Fig. 8.

A better understanding of the nature of this sharp rise will be had from examination of the data in Figs. 6 and 7. Here F was increased in steps to a high value and was then progressively decreased. In Fig. 6 (with the C_{23} acid on

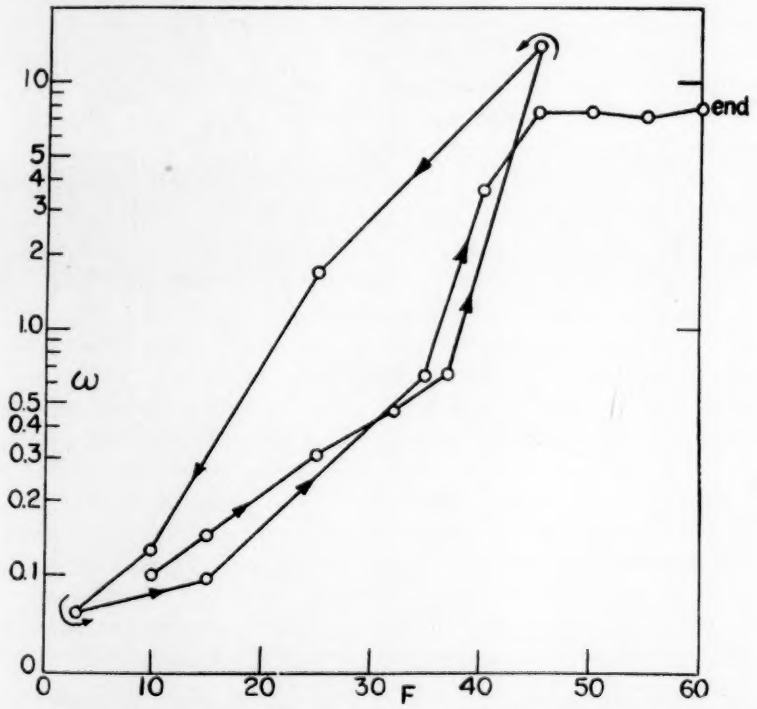

FIG. 6. Hysteresis effects observed with the C_{23} acid on 10^{-4}M Ba, pH 7.

10^{-4}M. Ba, pH 7) ω_f after rising slowly while F was raised to 35 underwent a twenty-fold increase when F was raised from 35 to 45. When F was decreased to 25 the value of ω_f was more than 5 times greater than had previously been found at the same value of F. Upon reducing the pressure to $F = 10$,

however, the value of ω_f decreased nearly to its initial value. As the pressure was raised again up to $F = 45$ the first ascending part of the curve was approximately reproduced.

Similar hysteresis curves were obtained with all the fatty acids on the water containing barium salts, pH 7. The hysteresis in the $\omega_f(F)$ curves seems to be roughly paralleled by appreciable but smaller hysteresis in the $(F\text{-}A)$ curves. Thus when the pressure was decreased the area of these films of the barium soaps did not increase as much as the corre-

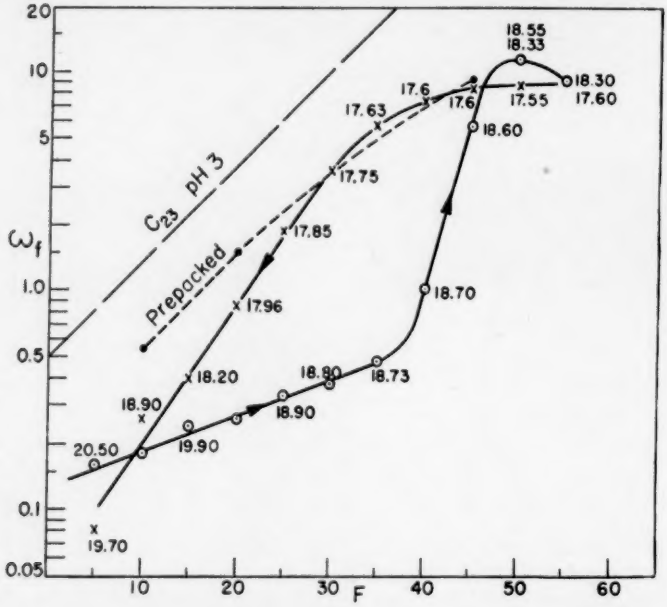

FIG. 7. Hysteresis effects shown by a monolayer of the C_{20} alcohol on distilled water pH 5.8. The curve marked "prepacked" was obtained after several cycles up to values of F not exceeding 45 dynes cm.

sponding decreases that occurred when the pressure was raised. On the other hand with the fatty acid films on water of pH 3 the $(F\text{-}A)$ curves for descending values of F usually coincided with the ascending values provided the maximum pressure was about 5 dynes/cm. less than F_c.

Hysteresis effects were also obtained with films of the C_{20} alcohol on distilled water, pH 5 as shown in Fig. 7. The

figures along the curve close to the observed points give the areas in sq. A per molecule. When there was any appreciable collapse of the film two figures are placed close to one point (at $F = 50$ and $F = 60$) to indicate the initial and final areas which were recorded at these pressures.

Other runs were made with the C_{20} alcohol in which the maximum pressure did not exceed $F = 45$. The hysteresis loop in this case had a much smaller area and after 2 or 3 alternations of pressure between $F = 10$ and $F = 45$ the area of the loop decreased to practically zero, giving the dotted line marked "Prepacked." For comparison the C_{23} pH 3 theoretical line of Fig. 3 is reproduced in Fig. 7. It is interesting that with this film several alternations of pressure caused the values of ω_f to rise to their highest values. There is, however, a large and permanent decrease in ω_f if the pressure is raised enough to produce much collapse.

All of these phenomena show that the evaporation resistance ω_f is a property of condensed monolayers which is extremely sensitive to internal changes in the monolayers, and should thus be of great value as a means for reaching a better understanding of the structure of condensed monolayers.

Figure 8 gives a number of curves which we have obtained for the barium soaps of fatty acids C_{16} to C_{21}. These were early experiments made under conditions which were not as carefully controlled as those we adopted later.

Mixed Films of C_{23} *Acid with Cholesterol.* As was pointed out in the opening paragraphs our experiments on evaporation resistances were originally started to find whether small traces of impurities in a high resistance film cannot cause a great decrease in resistance thus explaining the peculiar aging effects which Sebba and Briscoe attributed to polymerization of alcohol molecules. We therefore decided to use mixtures of the C_{23} acid with cholesterol a substance which gives a resistance so low that Sebba and Briscoe were not able to measure it. Figure 9 summarizes the results that we obtained. The full-line curve marked C_{23} gives new data for the C_{23} acid as part of this series of experiments. The dashed curve is a reproduction of the curve of Fig. 5 obtained by us at another time.

Three mixtures were studied containing 1 part of cholesterol to 1800 parts of C_{23} acid; 1 part of cholesterol to 60 parts of

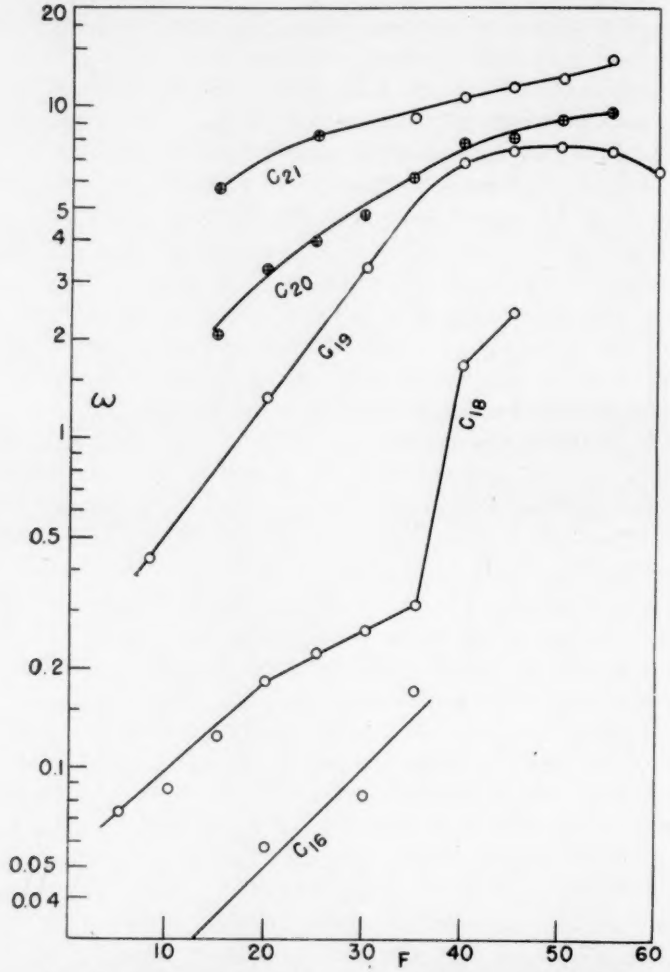

FIG. 8. Evaporation resistances of monolayers of fatty acids C_{16} to C_{21} on 10^{-4}M Ba, pH 7.0.

acid; and 1 part of cholesterol to 15 parts of acid. Figure 9 also shows the curve obtained from the cholesterol alone.

It is seen that the value of ω_f for cholesterol is by no means negligible. A monolayer of this substance decreased the ob-

served rate of evaporation about 30 per cent. As little as one part in 1800 of cholesterol in the acid decreased the value of ω_f by about 40 per cent. 1 part in 60 lowered the resistance to one-tenth at $F = 45$ but raised it 80 per cent. at $F = 25$.

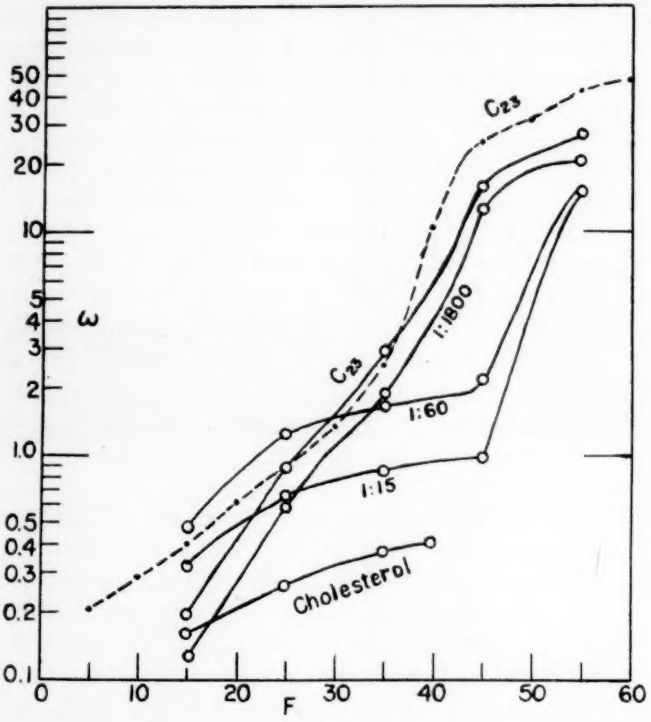

FIG. 9. Evaporation resistances of mixed films of C_{23} acid with cholesterol. The ratios marked on the curves give the parts by weight of cholesterol. Thus 1 : 15 means 1 part of cholesterol to 15 parts of the C_{23} acid. pH 5.8 25° C.

The upper parts of the curves shows a rapid rise suggesting that cholesterol gets squeezed out from between the fatty acid molecules.

These preliminary experiments prove that minute amounts of foreign substances may have very great effects on the resistances. The use of measurements of ω_f, which are easily made, thus promises to throw much light on the interactions between molecules in monolayers.

Mixed Films of Dihydroxystearic Acid and the C_{21} *Acid.* From theoretical considerations which will be discussed later we were led to the belief that a high resistance in the monolayer must depend upon an intense localized compressive force at a definite level or stratum in the monolayer. We thought then if we could add to the monolayer some molecules like dihydroxystearic acid which have an increased cross section in the middle of the chain we might obtain a high state of compression at this level. If too many molecules of this type were present it would interfere with the formation of the condensed film and produce an expanded film which would offer little resistance. These predictions from theory have been verified by the experimental data shown in Fig. 10.

The material used in experiment of Fig. 10 was the 9, 10 dihydroxystearic acid (DHC_{18}) obtained several years ago from Eastman. There are several modifications of this substance. The one that we used melted at 130° C. and is thus the high melting racemic form which can be made from oleic acid by treatment with permanganate. Beilstein gives the melting points of 132° and 95° for the high and low melting enantiomeric forms.

There are three sets of curves in Fig. 10. The lower five curves give ω_f as a function of F. The lowest curve near the bottom which is marked DHC_{18} refers to the dihydroxystearic acid. The value of ω_f was 0.04 and was practically independent of F. The topmost curve in Fig. 10 which has its own special scale of ordinates at the left is the area per molecule of this film on water. It is a highly expanded film occupying 78 sq. A per molecule at $F = 10$. It stands 45 dynes/cm. before very much collapse sets in, the area then being about 50.

The other curves in the lower part of Fig. 10 are marked C_{21}, 2, 5, and 10. The curve marked C_{21} refers to the monolayer of the pure C_{21} acid. The four figures 2, 5, and 10 on the other three curves give the number of parts by weight of the C_{21} acid for each part of the DHC_{18} acid in the film. The four curves marked C_{21}, 10, 5, and 2 which are in the middle level of Fig. 10 with a scale of ordinates on the left represent the areas per molecule for these mixed films. The C_{21} acid gives a broken curve like those shown in Fig. 4, and the curves

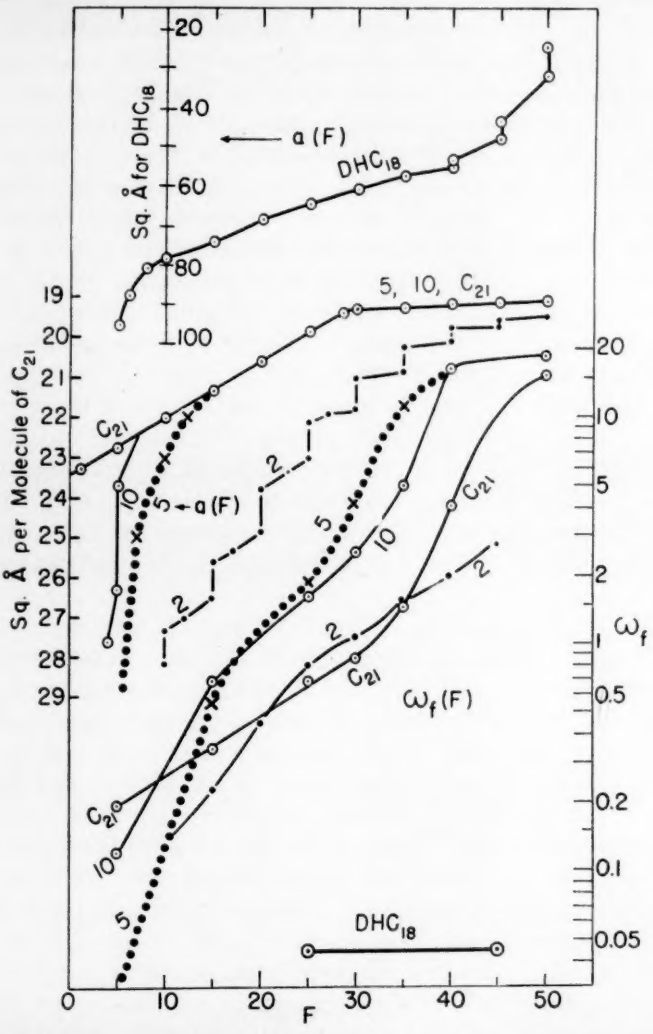

FIG. 10. Evaporation resistances and $a(F)$ curves for mixed films of C_{21} acid with dihydroxystearic acid (DHC_{18}). The numbers on the curves denote the parts by weight of the C_{21} acid for each part of the DHC_{18}. Note three scales of ordinates.

10 and 5 join this C_{21} curve at about $F = 8$ and 14 dynes cm.$^{-1}$ respectively. At lower values of F the areas are much larger. Thus a film which consists of one part with DHC_{18} acid and 10 parts of the C_{21} acid acts as an expanded film at very low pressures and gives a low resistance.

The area per molecule contributed by the DHC_{18} acid at $F = 8$ should be about 8 sq. A if the areas were additive. However, at a pressure of only $F = 7$ nearly all of this DHC_{18} acid is squeezed out and the area becomes practically that of the C_{21} acid. (Small differences of the order of 0.2 sq. A were observed but were considered to be not greater than the probable experimental error.) Above $F = 10$, ω_f increased rapidly to values about three times as great as that observed with the pure C_{21} acid in spite of the fact that most of the DHC_{18} acid must have been squeezed out of the monolayer. Still higher values of ω_f were obtained at $F = 30$ and 40 in curve 5 with the greater amount of the DHC_{18} acid. However, in this case the film remained expanded up to about $F = 14$ and up to this pressure ω_f was much lower than that for the pure acid.

With the proportion of the DHC_{18} acid increased to 1 : 2 the DHC_{18} acid was not completely squeezed out at even the highest pressures. There was a steady decrease in area at each value of F above 10 as shown by the broken lines of the $a(F)$ curve, marked 2. The presence of only 30 per cent. of the C_{21} acid causes rapid collapse of the film of the DHC_{18} even at low pressures while the pure DHC_{18} acid should withstand even $F = 50$. These data serve as good illustrations of the fact that small amounts of a foreign substance can cause collapse of a film that would otherwise stand high pressure.

Evaporation Resistances of Thicker Oil Films. In order to determine the diffusion resistance produced by thicker films of the hydrocarbon oils on the surface of water we spread duplex films of oxidized turbine oil. We also studied films of aroclor which is a mixture of chlorinated aromatic hydrocarbons (largely pentachlor diphenyl), used as a non-inflammable oil for transformers and condensers. In order to make these substances spread small amounts of highly oxidized oil were added. The technique of preparing and measuring the thickness of those films of indicator oils has already been

described.[10,11,12] The thickness of the duplex film spread on water can be varied within wide limits by altering the proportion of oxidized oil used, allowing the oil to spread on a free water surface. By compression between barriers the thickness can be increased to any desired degree. Thus it was possible to vary the proportion of oxidized oil without altering the thickness.

The evaporation resistance ω_f was measured by using the drying box and the results are shown in Fig. 11. The abscissas

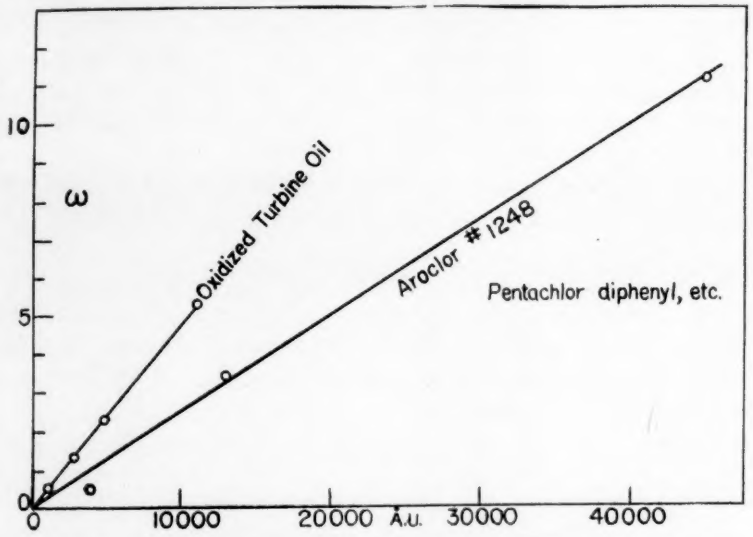

FIG. 11. Effect of duplex films of a hydrocarbon oil and of aroclor upon the evaporation of water.

represent the thickness of the duplex film in A units. The resistance increases in proportion to the thickness of the film and is entirely independent of the proportion of the oxidized oil needed to produce the spreading.

The value of ω_f/b_f for the oxidized oil is 4.7×10^4 sec. cm.$^{-2}$ while for the aroclor it is 2.54×10^4 sec. cm.$^{-2}$. Eqs. (14), (7), and (6) give

$$M/At = w_a/\omega_f = D_f w_f/b_f, \qquad (22)$$

[10] K. B. Blodgett, *J. Opt. Soc. Amer.*, **24**, 313 (1934 December).
[11] V. J. Schaefer, *J. Phys. Chem.*, **42**, 1089 (1938).
[12] I. Langmuir and V. J. Schaefer, *Chem. Rev.*, **24**, 181 (1939).

where M/At is the rate of evaporation of water through the film when the air above the film is completely dry, w_a is the vapor density of air saturated with moisture, w_f is the concentration of water vapor, in g. cm.$^{-3}$, in the oil film on the surface when saturated with water, D_f is the diffusion coefficient of water within the oil film, b_f is the thickness of the oil film, and ω_f is the evaporation resistance of the oil film that is given by the experiments by Fig. 11. By introducing the values of w_a, and w_f/b_f we find

$$D_f w_f = 4.1 \times 10^{-10}. \tag{23}$$

According to the data of International Critical Tables the solubility of water in hydrocarbons, such as petrolatum and lubricating oils, is of the order of 0.005 per cent., so that we may take $w_f = 5 \times 10^{-5}$ g. cm.$^{-3}$.

A general empirical equation for the diffusion coefficients of organic substances in liquids has been given by Thovert [13]

$$D = 8 \times 10^{-7}/(\eta M_C^{1/2}) \text{ cm.}^2 \text{ sec.}^{-1}, \tag{24}$$

where M_C is the molecular weight of the diffusing substance and η is the coefficient of viscosity of the solvent through which the diffusion occurs. Introducing $M_C = 18$ for water molecules we thus find

$$D = 1.9 \times 10^{-7}/\eta. \tag{25}$$

From this and the value of w_f, we find by Eq. (23):

$$\eta = 0.023 \text{ C.g.S.} \tag{26}$$

which is a very reasonable value for the viscosity of hydrocarbons.

We conclude that the observed value of ω_f/b_f from the experiments of Fig. 11 indicates that the evaporation resistance given by these thick films is wholly a diffusion phenomenon through the bulk of the oil and that there is no appreciable resistance associated with the upper or lower interfaces of the duplex film.

The resistance of an oil film having the thickness of a stearic acid monolayer (24 A) or an oleic acid monolayer (11 A) would amount to 0.011 or 0.005 sec. cm.$^{-1}$ respectively.

[13] M. J. Thovert, *Ann. de Phys.*, **2**, 369 (1914).

These may be compared with the values of ω_f calculated from Rideal's data for these two acids viz. 0.007 for the stearic acid and 0.019 for oleic acid. Our measurements for stearic acid at higher values of F (Fig. 3) have given $\omega_f = 1.2$ which is a hundred times greater than can be attributed to the diffusion resistance offered by the hydrocarbon layer. In the case of the C_{23} acid this discrepancy is of the order of 5,000 : 1.

Although the diffusion resistances of the hydrocarbons shown in Fig. 11 are very small for thicknesses comparable to those of monolayers, the resistances become very great (4700 sec. cm.$^{-1}$) for a layer of oil 1 mm. thick.

DISCUSSION OF EXPERIMENTAL RESULTS

Energy Barriers. Using Eq. (21) to summarize the results of the experiments on the fatty acids on acidified water which have given the highest values of ω_f, we may calculate the magnitude of the energy barrier, λ, by Eqs. (18) and (20). We find

$$\lambda/kT = 2.51 + 0.98F + 0.28n. \qquad (27)$$

If we want to express λ in calories per g. molecule at 20° C. we should replace kT by 582 calories. Thus we find that each increase in pressure of 1 dyne cm.$^{-1}$ increases the height of the barrier by 570 calories. An increase in the length of the hydrocarbon chain of one CH_2 increases the barrier by 163 calories.

The highest value of ω_f which we have observed, 62 sec. cm.$^{-1}$, corresponds to a condensation coefficient of $\alpha = 1.1 \times 10^{-6}$ and a total energy barrier of 8000 calories.

If we look upon the energy barrier, λ, as equal to the product of P and v_0 where P is the pressure that acts upon the water molecule of volume v_0, then we calculate from Eq. (27) that

$$P = 3340 + 131F + 374n \text{ atmospheres.} \qquad (28)$$

One of the common methods of determining the magnitudes of energy barriers involves measurement of the temperature coefficient of a reaction velocity. From Eqs. (20) and (18) we find

$$d \ln \omega_f/dT = - d \ln \alpha/dT = \lambda/kT^2. \qquad (29)$$

In July 1940 we made one experiment to measure the temperature coefficient of ω_f. A film of the C_{21} acid was spread upon dilute H_2SO_4 pH 3, in a trough surrounded by a large water bath so that the temperature could be changed.

TABLE IV.

Effect of Temperature on Evaporation Resistance. C_{21} *Acid on Dilute* H_2SO_4 *pH 3.*

F.	Observed Evaporation Rate, mg. in 5 min.		ω_f sec. cm.$^{-1}$		Ratio	
	28° C.	17° C.	28° C.	17° C.	Obs.	Calc.
25	317	135	0.30	0.43	1.43	1.40
35	271	110	0.51	0.79	1.56	1.42
45	72	36	4.50	4.71	1.05	1.48

With the water at 28° C., ω_f was measured at 25, 35 and 45 dynes cm.$^{-1}$ and then with $F = 15$ the temperature was lowered to 17° C. and measurements of ω_f were made with the same monolayer at the same series of pressures. The results are given in Table IV.

The rate of evaporation M/t is about 2.3 times greater at 28° than at 17°, but most of this increase is accounted for by the rise of vapor density w with temperature. The observed ratio of ω_f at 17° to that at 28° agrees roughly with the values in the last column calculated by Eq. (29) with values of λ/kT obtained from ω_f by Eqs. (18) and (20).

It is desirable that further more accurate measurements of temperature coefficient be made with various films using a much wider temperature range. Such measurements should serve as a check on the energy barrier theory and would indicate whether the exponential term in Eq. (20) should have a numerical coefficient other than unity.

Internal Stresses in Monolayers. In order to clarify our ideas regarding the structure of monolayers of fatty acids and alcohols, let us consider the behavior of a model.

We assume that we have a number of hydrocarbon molecules C_nH_{2n+2} subject to the following two constraints.

1. One end of each molecule (for example the carbon atom of a terminal CH_3 radical) must be located on a plane B.

2. All the remainder of these molecules must remain on one side (say the upper side) of the plane B.

Let the number of such molecules per unit area of the plane be σ. The area per molecule a is then defined by

$$a = 1/\sigma. \tag{30}$$

We assume also that the molecules are subject to the forces of interaction (van der Waals forces and repulsive forces) responsible for the ordinary volume properties of hydrocarbons such as compressibility, crystal structure, heats of evaporation, heat of fusion, etc.

We wish now to consider how the molecules behave as σ progressively increases. With low σ the molecules behave as an ideal 2-dimensional gas, and there must be a surface pressure given by

$$F = \sigma kT \qquad \text{or} \qquad Fa = kT. \tag{31}$$

At higher σ, there will be deviations from this ideal law.

At sufficiently low temperature the attractive forces (van der Waals) between the molecules will cause them to condense as a 2-dimensional liquid, so that as σ increases F will stay constant (2-dimensional vapor pressure) until the liquid phase covers the surface and a has then a much lower value than for a gaseous film. The longer the chain, that is the greater the value of n, the lower the temperature at which this liquid phase can form.

Let us examine the factors that determine the value of a for the molecules in this 2-dimensional liquid phase. We can best understand the problem of considering the analogous 3-dimensional cause.

An unconstrained 3-dimensional mass of liquid hydrocarbon assumes a spherical form (surface tension). It has been shown [14] that the same tendency is manifest down to single molecules in the vapors of long chain hydrocarbons, whose molecules take approximately the form of spheres with a surface energy of about 34 ergs per cm.^{2}.

We thus see that the 2-dimensional liquid phase of our model will be drawn together with forces of the order of 2γ where γ is the normal surface tension (ca. 30 dynes/cm.), until some other force prevents further contraction. The film (for large values of n) thus tends spontaneously to become a

[14] I. Langmuir, *Proc. Roy. Soc.*, **170A**, 9 (1939); *Chem. Reviews*, **6**, 475 (1929).

condensed film with a comparable to $20\,A^2$ per molecule. Here the repulsion forces between the molecules and the thermal agitation bring about a balance with the surface tension forces.

If the temperature is lower than that of the freezing point of the 3-dimensional hydrocarbon, the same forces that produce crystallization should cause the molecules of our model to arrange themselves exactly as they do in the normal hydrocarbon crystals, since our two constraints are now only those that are actually present in ordinary crystals.

It is known that higher hydrocarbons crystallize (orthorhombic or hexagonal) with their molecules arranged in planes (basal planes) with the zig zag hydrocarbon molecules having axes perpendicular to the basal plane ($\theta = 90°$). The area per molecule (measured on this plane) is $a = 18.3\,A^2$.

It is known from x-ray studies [15] that even for changes of temperature produced by liquid air there is no appreciable coefficient of thermal expansion in the direction of the axis of the chains indicating that the carbon bond angle of 109° remains independent of temperature. Under these conditions the zig-zag molecules are in step with one another.

If all the chains, while parallel to one another, are tilted so that θ is 63° 10′ the molecules are again in step so that (except near the ends of the molecules) the relationship of any CH_2 group to its neighbor in adjacent molecules is the same as for the original case of $\theta = 90°$. The area per molecule of basal plane is then $a = 18.5/\sin\beta = 20.51\,A^2$.

The molecules are again in step if $\theta = 44° 40'$ and $a = 26.0\,A^2$.

In our model let us now assume that we have a third constraint that holds the terminal CH_3 groups in the B plane in a regular surface lattice like that in the basal plane of a 3-dimensional hydrocarbon crystal but that we can continuously change the scale of the lattice altering the value of a.

It is evident that when a has the definite values 18.30, 20.51, 26.0, etc. which permit the molecules to be in step the free energy is a minimum.

If we made a slightly less than one of these equilibrium values, the molecules are abnormally crowded against one

[15] A. Müller, *Proc. Roy. Soc.*, **114A**, 542 (1927).

another and thus a large compressive force F must be applied to decrease a. In order to increase a an internal tension (negative value of F) must be applied. The situation is quite analogous to a liquid under negative pressure. Negative pressures can exist only if the vapor phase is prevented from forming. In our model our third constraint will have this effect.

Between the minima corresponding to 18.5, 20.5, 26.0 there must be maxima in potential energy. Too great an increase in a above one of the minimum values will tend to produce a progressive breakdown of the crystalline structure.

An estimate of the magnitude of the energy involved in these changes in area may be made from the latent heat of fusion of hydrocarbons. Each additional CH_2 increases the heat of fusion by 60° calories per mole.[16]

Let us now consider the case where the CH_3 terminal groups in the plane B are replaced by active groups such as carboxyl or carbinol and that the plane B is a surface of water. The water then automatically gives the Constraints 1 and 2 which we have previously had to assume.

The water tends to squeeze in between the active groups or heads and force them apart. The thermal agitation of the heads may, if n is small enough, be able to cause the heads to spread out on the surface as a gas except in so far as this is opposed by the tendency of the liquid hydrocarbon film to draw together. This theory of expanded films accounts quantitatively for most of their properties.

At higher pressures or larger values of n, where the films are condensed we may still consider that the interactions between the heads and with the underlying water gives a resultant surface pressure F_H which will be a function of a. The observed external surface pressure F which acts on the film is thus

$$F = F_R + F_H, \tag{32}$$

where F_R is the pressure exerted by the hydrocarbon chain as already considered. Both F_R and F_H are functions of a, but functions of very different kind.

[16] I. Langmuir, *Jour. Chem. Phys.*, 1, 756, Pg. 772 (1933).

The *area per molecule a must be the same for both parts of the film.* Thus if the heads require an area which is a little greater than values 20.5 A^2 which gives a minimum energy for the chains then these chains also must occupy a larger area and thus F_H may take large *negative* values. This means that F_H may be much greater than the observed pressure F. According to this theory F_H can increase greatly as n increases.

We have seen that the high values of ω_f we have found indicate energy barriers of large magnitude (8000) which increase by 160 cals. for each additional CH_2. The internal localized compressive and tensile stresses within monolayers may in part explain the large evaporation barriers. However, this factor alone is not sufficient.

Equation (28) shows that an increase in F of 1 dyne cm.$^{-1}$ gives an increment to the barrier corresponding to a pressure P of 131 atmospheres acting upon the volume of a water molecule, 30 A^3. Since this molecule has a length of at least 4 A the pressure of 131 atmospheres would have to be exerted throughout a layer of this thickness to give the required increment in the barrier. This, however, would give an increase in F of $4 \times 10^{-8} \times 1.3 \times 10^8$ or 5.2 dynes cm.$^{-1}$, which cannot balance the applied surface pressure of 1 dyne cm.$^{-1}$.

The pressures P given by Eq. (28) are therefore not pressures that exist *a priori* within a certain stratum of the monolayer, but are mainly local forces brought into existence by the presence of the water molecule.

Crystal-like Properties of Condensed Monolayers. We have already seen that the alternating increases and decreases in F_c according as n is odd or even are characteristic of a crystalline state of the monolayers. There are many other facts that support this conclusion. It was shown by Cary and Rideal [17] and Langmuir [18] that stearic acid monolayers even at $F = 0$ are stable on water at pH 2 only at temperatures above 28° C. Theoretically a monolayer of this acid at $F = 30$ would be stable only at temperatures above 80° C. Thus all the compressed fatty acid monolayers we have studied are metastable. It is undoubtedly the interlocking of the hydrocarbon chains in the condensed films that holds them in the monolayer even

[17] A. Cary and E. K. Rideal, *Proc. Roy. Soc.*, **109A**, 301, 318, 331 (1925).
[18] I. Langmuir, JOUR. FRANK. INST., **218**, 168 (1934).

at high values of F in spite of their inherent thermodynamic instability.

In the theory of expanded films [16] it was shown that the kink in the $F(a)$ curve was caused by the sudden formation of micelles at a critical value of F. As F increased the proportion of micelles increased until finally when a part of the $F(a)$ curve was reached which corresponds to the portion AB in Fig. 4, the micelles formed a continuous structure.

The heat of formation of the micelles increased by 243 calories per mole for each additional CH_2. This is about 40 per cent. of the heat of fusion of hydrocarbons indicating that the crystallization is not perfect. This difference is to be expected since a is not the same as in the normal crystalline state.

We must therefore consider that the condensed films both in the AB and BC portions of the curves have their molecules arranged in an imperfectly crystalline form. Presumably the hydrocarbon chains are mostly in step with their neighbors but the angle of tilt θ and the corresponding azimuth angles are constant only within limited small domains that are continually fluctuating in position and magnitude.

We can now advance the hypothesis that the presence of a water molecule causes a local breakdown in crystal structure that affects a relatively large number of neighboring molecules. Thus many molecules coöperate in producing the barrier and the magnitude of the barrier should depend on the length of the chain.

To produce this effect it is not essential that the water molecule should lie between the hydrocarbon chains of neighboring molecules. It is more likely that the heads, which are under a high compressive stress F_H are themselves forced into a lattice-like or close-packed arrangement which determines the possible arrangements of the tails. A water molecule inserted among the heads can cause a disruption of the surface lattice which in turn causes many of the hydrocarbons to get partly out of step or forces a change in the angle of tilt.

The water molecule which produces such a widespread effect must naturally be subjected to intense opposing forces which may well be equivalent to the pressure P of Eq. (28).

Absence of Kinks in $\omega_f(F)$ Curves at F_B. In view of the presence of definite kinks B in the $F(a)$ curves of the acids and alcohols, Fig. 4, it is natural to expect kinks in the $\omega_f(F)$ curves at the same values of F. The surface viscosities of monolayers of alcohols have been found [19] to show sudden increases at critical values of F which agree reasonably well with F_B.

It is a remarkable fact, however, that the $\omega_f(F)$ curves that we have obtained show no kinks that coincide with the values of F_B in Tables I, II, and III. For example, the fatty acids C_{18}, C_{20} and C_{23} show very sharp kinks in their $F(a)$ curves at 24, 27, and 30 dynes per cm., but there are no indications of kinks in the curves of Fig. 3. On the other hand the $\omega_f(F)$ curve of Fig. 5 shows a sharp rise at $F = 37$ but none at $F = 30$. Fig. 6 shows a sharp kink at $F = 38$ but Table III gives only a very slight kink at $F = 10$ in the $F(a)$ curve. The curve of $\omega_f(F)$ for the C_{20} alcohol (Fig. 7) is a straight line from $F = 5$ to $F = 35$ although there is a very sharp kink at $F_B = 17$ dynes cm.$^{-1}$ for the same substance shown in the $F(a)$ curve, in Fig. 4.

The marked changes in ω_f observed in the hysteresis experiments, Fig. 7, that appear to be associated with small changes in area; and the very great sensitiveness of ω_f to small residual admixtures shown in Figs. 9 and 10 are hard to reconcile with the absence of effects resulting from the fundamental changes in structure presumably associated with the kink at B.

Certainly much more experimental and theoretical work needs to be done before these effects can be well understood.

[19] L. Fourt and W. D. Harkins, *Jour. Phys. Chem.*, **42**, 897 (1938).

A MODIFIED TREATMENT OF THE ITERATIVE METHOD.

BY

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One of the most powerful and useful methods for the determination of the natural frequencies of a vibrating system is the iterative method. This paper deals with a simple modification of the iterative method leading to the same accuracy in fewer steps with a consequent saving in time and labor.

The equations of displacement of a system in a natural mode of vibration may be expressed [1]

$$\begin{aligned} x_1 &= \lambda m_1 G_{11} x_1 + \lambda m_2 G_{12} x_2 + \cdots + \lambda m_n G_{1n} x_n, \\ &\cdot \\ &\cdot \\ &\cdot \\ x_n &= \lambda m_1 G_{n1} x_1 + \lambda m_2 G_{n2} x_2 + \cdots + \lambda m_n G_{nn} x_n, \end{aligned} \tag{1}$$

where x_k is the displacement at point k

m_k is the mass at point k

G_{kj} is the influence coefficient expressing the displacement of the system at point k due to a unit load at point j

and λ is the square of the natural frequency of vibration.

In matrix form, equations (1) may be written [2]

$$\{x\} = \lambda GM\{x\}, \tag{2}$$

[1] Den Hartog, "Mechanical Vibrations," McGraw-Hill Co.

[2] Frazer, Duncan, and Collar, "Elementary Matrices," Cambridge University Press.

where $\{\ \}$ hereafter designates a one column matrix. That is

$$\{x\} = \begin{Bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_n \end{Bmatrix},$$

$$M = \begin{Bmatrix} m_1 & 0 & \cdots & 0 \\ 0 & m_2 & & \\ \cdot & & \cdot & \\ \cdot & & & \cdot \\ \cdot & & & \\ 0 & & & m_n \end{Bmatrix}$$

and G is the matrix of the influence coefficients. Associated with equation (2) are n characteristic functions $\varphi^{(k)}(x)$ and corresponding characteristic numbers λ_k, $(k = 1, 2, \cdots, n)$ each of which satisfies equation (2), that is

$$\{\varphi^{(k)}\} = \lambda_k GM\{\varphi^{(k)}\}. \tag{3}$$

These characteristic functions satisfy the following relations[2]

$$\left.\begin{aligned} [\varphi^{(j)}]M\{\varphi^{(k)}\} &= 0, \quad k \neq j \\ [\varphi^{(k)}]M\{\varphi^{(k)}\} &= 1 \end{aligned}\right\} \tag{4}$$

which express the orthogonal and normal properties respectively of the characteristic functions. The brackets $[\ ]$ designate the one-row matrix

$$[\varphi_1^{(k)}, \varphi_2^{(k)}, \cdots, \varphi_n^{(k)}].$$

In the method of iteration, the starting point is an arbitrary one column matrix $\{\psi\}_0$ which may be expressed in terms of the characteristic functions in the following manner

$$\{\psi\}_0 = a_1\{\varphi^{(1)}\} + a_2\{\varphi^{(2)}\} + \cdots + a_n\{\varphi^{(n)}\}. \tag{5}$$

By successive pre-multiplications of (5) by GM, and using

(4), we get

$$\left.\begin{aligned}
\{\psi\}_1 = GM\{\psi\}_0 &= \frac{a_1\{\varphi^{(1)}\}}{\lambda_1} + \frac{a_2\{\varphi^{(2)}\}}{\lambda_2} \\
&\quad + \cdots + \frac{a_n\{\varphi^{(n)}\}}{\lambda_n} \\
&\cdots \\
\{\psi\}_r = GM\{\psi\}_{r-1} &= \frac{a_1\{\varphi^{(1)}\}}{\lambda_1{}^r} + \frac{a_2\{\varphi^{(2)}\}}{\lambda_2{}^r} \\
&\quad + \cdots + \frac{a_n\{\varphi^{(n)}\}}{\lambda_n{}^r} \\
\{\psi\}_{r+1} = GM\{\psi\}_r &= \frac{a_1\{\varphi^{(1)}\}}{\lambda_1{}^{r+1}} + \frac{a_2\{\varphi^{(2)}\}}{\lambda_2{}^{r+1}} \\
&\quad + \cdots + \frac{a_n\{\varphi^{(n)}\}}{\lambda_n{}^{r+1}}.
\end{aligned}\right\} \tag{6}$$

The usual manner of obtaining the lowest characteristic value λ_1, is by taking the ratio of homologous elements in the matrices $\{\psi\}_r$ and $\{\psi\}_{r+1}$. This leads to

$$\frac{\{\psi\}_r}{\{\psi\}_{r+1}} = \lambda_1 \frac{a_1\{\varphi^{(1)}\} + \left(\frac{\lambda_1}{\lambda_2}\right)^r a_2\{\varphi^{(2)}\} + \cdots + \left(\frac{\lambda_1}{\lambda_n}\right)^r a_n\{\varphi^{(n)}\}}{a_1\{\varphi^{(1)}\} + \left(\frac{\lambda_1}{\lambda_2}\right)^{r+1} a_2\{\varphi^{(2)}\} + \cdots + \left(\frac{\lambda_1}{\lambda_n}\right)^{r+1} a_n\{\varphi^{(n)}\}}, \tag{7}$$

where $\lambda_1 < \lambda_2 < \cdots < \lambda_n$. It is evident that the limit reached as r becomes larger is λ_1. We may also conclude that λ_1 lies between the smallest and the largest ratio of homologous elements after a finite number of iterations. In equation (7) there appears the ratio of λ_1 to the higher λ's raised to a power which increases with r. Hence it is clear that the success of the method depends upon the degree of separation of the λ's.

However, if instead of (7) we take the following ratio

$$\frac{[\psi]_r M\{\psi\}_{r+1}}{[\psi]_{r+1} M\{\psi\}_{r+1}} = \frac{m_1 x_1{}^{(r)} x_1{}^{(r+1)} + m_2 x_2{}^{(r)} x_2{}^{(r+1)} + \cdots + m_n x_n{}^{(r)} x_n{}^{(r+1)}}{m_1 x_1{}^{(r+1)^2} + m_2 x_2{}^{(r+1)^2} + \cdots + m_n x_n{}^{(r+1)^2}}, \tag{8}$$

which by virtue of relations (4) is equal to

$$\lambda_1 \frac{a_1^2 + \left(\frac{\lambda_1}{\lambda_2}\right)^{2r+1} a_2^2 + \cdots + \left(\frac{\lambda_1}{\lambda_n}\right)^{2r+1} a_n^2}{a_1^2 + \left(\frac{\lambda_1}{\lambda_2}\right)^{2r+2} a_2^2 + \cdots + \left(\frac{\lambda_1}{\lambda_n}\right)^{2r+2} a_n^2},$$

the ratios of λ_1 to the other λ's are raised to powers at least double what they were in (7) and consequently the approximation to λ_1 is considerably better. We note that (8) gives a lower bound to the value of λ_1.

The physical interpretation of (8) is readily apparent.[3] It amounts to an application of Rayleigh's Principle in which the deflection $\{\psi\}_r$ is used as a loading to get the deflection $\{\psi\}_{r+1}$.

As an example,[2] consider the problem of finding the lowest frequency of vibration of a system which has for its matrix GM the form

$$\begin{bmatrix} 2 & 2 & 2 \\ 2 & 5 & 5 \\ 2 & 5 & 11 \end{bmatrix}.$$

Starting with an arbitrary $\{\psi\}_0 = \{1, 1, 1\}$, we find successively

$$\{\psi\}_1 = 18\{0.33, 0.67, 1\},$$
$$\{\psi\}_2 = 18 \times 15\{0.26, 0.60, 1\},$$
$$\{\psi\}_3 = 18 \times 15 \times 14.53\{0.257, 0.587, 1\},$$

from which $\lambda_1 \doteq \frac{\{\psi\}_2}{\{\psi\}_3} = 0.0688$ by the usual method. If however we make use of equation (8) instead of (7), then we obtain

$$\lambda_1 \doteq \frac{1}{14.53} \frac{(.26)(.257) + (.6)(.587) + (1)(1)}{(.257)^2 + (.587)^2 + (1)^2},$$

which leads to a numerical value for λ_1 equal to 0.06921. The exact value is 0.06929. Thus it is clear that the modified method leads to a closer approximation.

[3] Temple and Bickley, "Rayleigh's Principle," Oxford Press.

A PRELIMINARY SPECTROGRAPHIC STUDY OF NORMAL AND ARTHRITIC HUMAN BLOOD.*

BY

JOSEPH SAMUEL HEPBURN, CLARENCE A. HALL AND J. A. DOANE.

In this research, blood was drawn from the median basilic vein or the median cephalic vein into a sterile test tube and permitted to coagulate spontaneously. The coagulum and the serum were transferred to a quartz dish, dried at a temperature of 100° to 110° C., and reduced to ash at a low red heat in a muffle furnace. The ash was subjected to spectrographic analysis by exposure for 4 minutes to a direct current arc at 15 amperes from a 250-volt line in conjunction with graphite electrodes. A Gaertner quartz spectroscope of the Litrow type was used, and the resulting spectrum in the range 2500–3700 Angstrom units was recorded on an Eastman number 33 plate. Examination was made of samples of blood from 40 normal individuals and from 40 arthritic patients in the Arthritic Clinic of the Hahnemann Hospital. The blood of each person was examined separately. For the samples of blood, we are indebted to Drs. Peter J. Warter and George P. Miley and to Mr. Richard S. Oakey, Jr.

The following elements were common to all samples: Sodium, potassium, calcium, magnesium, iron, copper, aluminium, phosphorus, and silicon. The amount of silicon may have been misleading on account of the use of quartz dishes. The aluminium was high in 5 of the arthritic bloods. The amount of phosphorus was slightly less in the arthritic bloods than in the normal bloods. Nickel was present in 9 of the samples of normal blood.

* From the Hahnemann Research Foundation and the Department of Chemistry of The Hahnemann Medical College and Hospital of Philadelphia.

Detecting the Saboteur Static Electricity in Gasoline Fires.—ROBIN LEACH. (*Electrical Engineering*, Vol. 61, No. 10.) Two interesting examples of fires traced to static electric origins are cited by the author and explained, to illustrate an investigator's problems, his explorations for the facts, and his recourse to science for supporting evidence, in attempting to ascertain the probable causes for the ignition of inflammable gasoline vapor-air mixtures wherefrom the burning resulted in extensive secondary damages. Both examples relate to fires that were started during the refilling of underground gasoline storage tanks at garages. The first case of fire occurred at a privately owned filling station on an estate. The very unusual situation of the tank being unwittingly insulated from the ground provided a rational basis for concluding, with a reasonable degree of certainty, that a spark from the discharge of the electrified tank through the dielectric to ground caused the ignition of the highly inflammable gasoline vapor-air mixture. The second example relates to a fire at a commercial filling station on a large garage property. Here the fire occurred as the result of another very uncommon situation of a still different kind, and of a violation of well-established safety recommendations. The storage tank itself was quite well grounded, but no attempt had been made to ground the tank truck by either a ground wire or a drag chain. It was probably believed—if, indeed, any thought was given to the subject at all—that the grounding of the truck had been accomplished through the "ground wires" interwoven in the fill hose. But, the hose nozzle was effectively insulated from ground by the high dielectric property of the intervening films of gasoline and metallic oxides, and, therefore, the tank truck and its connected hose were unknowingly insulated from ground—a condition which, during the handling of gasoline, is at all times most dangerous. From these two and many other casualties from gasoline fires and explosions investigated by the author, he has found repeatedly that the so-called "inexplicable mysteries" of their origin generally dissolve into the commonplace when exposed to the illuminating facts and data revealed from an investigation of every pertinent channel of engineering knowledge and science by persistent, painstaking, and understanding research and study.

R. H. O.

INSOLATION IN THE POLAR ATMOSPHERE.

BY

ARNOLD COURT,

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Perpetual sunshine—24 hours a day, 365 days a year, forever—can be found within 2,800 miles of New York City, but as yet no promoter has built a hotel or begun to advertise the area in competition to Palm Springs or Miami Beach. Nor is anyone likely to do so in the near future, because this sunny region is in the vicinity of the North Pole; specifically, about 310 miles straight up, over the Pole.

This perpetual sunshine is actually the region of space outside the earth's shadow, which is closest to the earth over the poles, farthest in equatorial regions (Fig. 1). Over New York City, the outer limit of the earth's shadow, and thus the lower limit of the region of perpetual sunshine, is about 8,800 miles straight up; over the equatorial regions it is around 860,000 miles.

While perpetual sunshine more than 300 miles above the polar snows may be an interesting phenomenon, it is of little importance to astronomers, geographers, physicists, or meteorologists. But it helps emphasize a far more significant, but equally little known, fact: the amount of sunshine received in the polar atmosphere increases rapidly with height above the surface. For instance, throughout most of the polar regions there is one more month of continuous, 24-hour sunshine at a height of around 25 km. (15 miles) than there is at the surface. And, correspondingly, at the same level there is approximately one month less during which no sunshine whatever is received.

These facts, and others of considerable interest, can be seen readily on a graph (Fig. 3) of regions with no sunshine and with constant sunshine. Construction of this diagram resulted from studies undertaken as part of the analysis of meteorological results obtained during 1940 and 1941 at Little America III (78° 28′ S., 164° 55′ W.), the West Base of the

U. S. Antarctic Service (1), and especially in an effort to explain the wide (40° C.) annual variation in stratosphere temperatures which was observed there (2).

Distribution of the regions of continuous, 24-hour sunshine for a given day is shown in Fig. 1, in which the diagonal rulings

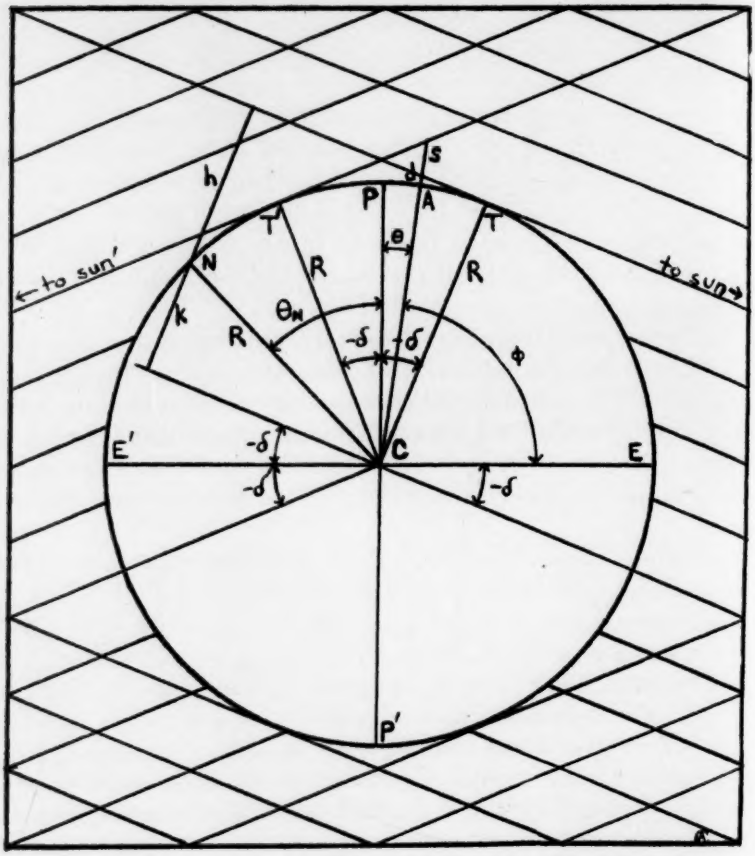

FIG. 1.

represent rays of light from the sun at noon (coming from lower right) and midnight (coming from lower left) for points on the great circle *PEP'*, some time in December. Regions where both sets of lines are present have 24-hour sunshine: the Antarctic, and a broad cone above the Arctic. A small surface

area in the Arctic receives no sunshine whatever, but above any point A in it there is sunshine at "noon" only at a height d and continuous sunshine even at midnight at and above a height s.

The sun's declination δ is taken as negative since it is in the southern hemisphere, and the co-latitude θ is considered to be, like the latitude ϕ, positive in the northern hemisphere, negative in the southern. Then,

$$\cos [(-\delta) - \theta] = \frac{CT}{CA + d} = \frac{R}{R + d}$$
$$d = R \sec (\theta + \delta) - R$$
$$d = R \operatorname{exsec} (\theta + \delta).$$

Likewise,

$$\cos [(-\delta) + \theta] = \frac{CT'}{CA + s} = \frac{R}{R + s}$$
$$s = R \sec (\theta - \delta) - R$$
$$s = R \operatorname{exsec} (\theta - \delta).$$

In addition, the shortest distance h to the constant sunshine regions can be determined for any point N, within or without the darkness region:

$$h + k = CT = R.$$

But

$$k = CN \sin \{90^\circ - [\theta_N + (-\delta)]\}$$
$$= R \cos [\theta_N + (-\delta)].$$

So

$$h = R - R \cos (\theta_N - \delta)$$
$$= R[1 - \cos (\theta_N - \delta)]$$
$$= R \operatorname{vers} (\theta_N - \delta).$$

These formulæ are, however, only first approximations, and must be corrected for two things: refraction, and the apparent diameter of the sun. Since the sun appears to be $32'$ across, when the "bottom" seems to one observer to be just touching the horizon, the "top" is just about to vanish below the horizon of another observer some 37 miles to the eastward. Tables of the sun's position refer to its center, so to δ must be added $16'$ to determine the direction of the ray of light from the upper limb. Technically, there should also be a correction for parallax, because the sun's direction is not exactly the same

from one place on earth to the next. Actually, the parallax correction is about 0′ 9″, less than the variation during the year in the apparent diameter of the sun, so it is neglected.

Much more difficult to determine is the amount of refraction, or the amount by which a ray of light is bent in entering the progressively denser layers of the atmosphere. It depends on the refractive index, which varies directly with the density of the air, which in turn is directly proportional to the pressure and inversely proportional to the temperature. But the variation of temperature with height changes constantly and is very irregular, so that it cannot be represented simply enough to use in a formula, and the pressure depends in part on the temperature.

Since the effect of these variations is very slight for rays coming in almost perpendicular to the atmosphere, and is very much greater for rays entering almost parallel to the atmospheric layers, astronomers have been able to evolve very satisfactory, although not rigorously exact, formulæ for determining the amount of refraction for all angles of incidence except those close to the horizontal. There, they agree (3), the atmospheric structure is so irregular that computation is fruitless, and better results can be obtained from direct observations. Several tables of the amount of refraction under varying conditions have been prepared; one of the best is that adapted by the Bowditch's American Practical Navigator (4) from original tables computed by the great Friedrich Bessel a century ago.

Horizontal refraction is usually considered to be 34′ in computing tables of sunrise, sunset, or sunshine duration, so that, since the sun's apparent semidiameter is 16′, the total correction is 50′; i.e., the actual time of sunset comes when "the true position of the sun's center is about 50′ below the horizon" (5). In passing, it may be mentioned that although, according to Kimball (6), general practice in America and Europe considers the sun to set at the instant when its *upper limb* is no longer visible, British usage (7) considers sunset to occur when the *center* of the sun appears to be on the horizon. Sunrise computed on this basis would come a little more than a minute later (in most latitudes) than according to American standards, sunset an equal amount earlier, thus making a

difference of more than two minutes in the theoretical length of day.

Because the amount of refraction depends on the angle at which a ray of light strikes an atmospheric layer and also upon the density of that layer, the refraction correction is greatest for low temperatures, since then the air is most dense. Bessel's tables, as given in Bowditch, provide corrections for deviation of surface atmospheric pressure and temperature from the values for which the table is computed. The following brief tabulation of the amount of horizontal refraction (in minutes of arc) at selected temperatures and pressures has been extracted from Bowditch:

inch	− 4° F.	14° F.	32° F.	50° F.	mbs.
30.00	41.17	39.42	37.85	36.33	1015.9
29.53	40.56	38.81	37.24	35.72	1000.0
29.00	40.05	38.30	36.73	35.21	982.1
	− 20° C.	− 10° C.	0° C.	10° C.	

In computing the time of sunrise and sunset at the surface and in the upper atmosphere of polar regions, a mean surface pressure and temperature must be assumed. As can be seen from the table, the pressure correction is small compared with that for temperature, and temperature is the element which varies most. But since the temperature desired is that of the air just at sunset, it is probably adequate to assume a temperature of freezing, with a pressure somewhat lower than normal. In the following computation, horizontal refraction has been taken as 37′, to which must be added 16′ for the sun's semi-diameter, so that it is assumed that in polar regions sunset occurs when the true position of the sun's center is 53′ below the horizon.

In considering the time of sunset at an elevated point in the atmosphere, there is still another refraction correction. Rays from the setting sun, having been refracted by 37′ in reaching the surface, will be refracted again as they continue just tangent to the surface and then, as the earth curves away from them, go on upward through the atmosphere. Obviously, by the time the ray, much weakened of course, emerges from the atmosphere, it will have been deflected by another 37′, so its direction will have changed by 1° 14′.

Just how this bending is distributed along the ray's path depends on the atmospheric structure, which is too complex to

give a simple answer. However, Smart (8) assumes that "40 miles may be regarded as the limit beyond which the air is ineffective in producing any appreciable refraction." No reason is given for using this value, but presumably it is connected with the fact that the earth's twilight arch has not been observed above 40 miles.

Above 65 km. (39 miles) an outbound ray may be considered to have suffered the full double bending, so that, in computing duration of sunshine at heights above 65 km.,

$$\delta = \delta' + 16' + 1^\circ\,14'.$$

The sign of δ', the sun's declination, depends on the season and is used just as given in the Ephemeris, as long as conventional signs are used on ϕ and θ. The corrections for semidiameter and double horizontal refraction have the same sign as ϕ and θ. The formulæ then become (above 65 km.)

$$d = R\,\text{exsec}\,(\theta + \delta' + 1^\circ\,30')$$
$$s = R\,\text{exsec}\,(\theta - \delta' + 1^\circ\,30').$$

The external secant (i.e., secant $-$ 1) function varies from zero at 0° to infinity at 90°, and if $y = a\ exsec\ x$ is graphed on rectangular coördinates, the curve resembles a parabola, except in the upper reaches. However, $exsec\ x = (1/cos\ x) - 1$, and since the first two terms of the Maclaurin series for the cosine are $1 - \frac{1}{2}x^2$, to a first approximation, and except for large angles, the external secant varies directly as the square of its angle. Thus, on coördinates of x and $\sqrt{y}$ the curve $y = a\ exsec\ x$ becomes almost a straight line. Such coördinates, latitude against square root of height, were chosen for Fig. 3, which essentially shows a series of graphs of the variation with latitude of the heights d and s for certain selected values of δ.

There remains to be determined just how the second bending of 37′ is distributed between the surface and 65 km. Theory is of no greater avail here than in the original consideration of the horizontal refraction, and recourse again must be made to observed values. Curves of the actual vertical distribution of density, computed from observed free-air temperatures and pressures (9) can be approximated, in great part, by a parabola. Consequently, a straight line drawn in Fig. 3

from the 65 km. level, where a correction of 1° 30′ is used, to the surface, where the total correction is only 53′, should approximate the true variation in the amount of refraction, certainly within the limits of the diagram itself.

For Fig. 3, the values of d and s were computed for every 2° of latitude from the Pole to 60°, and for solar declinations half a month apart throughout the year. The line connecting the s points for the maximum midwinter declination ($-$ 23° 27′ + 1° 30′) marks the lower limit of the region of all-year, perpetual sunshine, while the line through the corresponding d points is the upper limit of the region in which at least one day a year has no sunshine at all, or the lower limit of the region in which some sunshine is received on every day of the year.

Other lines have been drawn parallel to these, one pair through the values for the declination occurring half a month before and after the solstice, other pairs for declinations progressively half a month earlier and later, and so on to the equinoxes, at which the d lines, representing regions with no sunshine, disappear. The s lines continue on to the summer solstice, the final line marking the lower limit of the region in which 24-hour sunshine ever occurs, even for one day.

To aid in estimating the effect of this distribution of solar radiation in the polar atmosphere, a line has been added showing the percent of the earth's surface included inside any latitude circle. The area A which would be cut off from a sphere of radius R by a plane at a distance h from the pole (which plane intersects the sphere along a small circle, corresponding to a latitude circle of co-latitude θ) is given by

$$\begin{aligned} A &= 2\pi Rh = 2\pi R(R - R\cos\theta) \\ &= 2\pi R^2 \operatorname{vers}\theta. \end{aligned}$$

Since the total area of the earth is $4\pi R^2$, the percent of that surface included within a latitude parallel, at co-latitude θ, is

$$\begin{aligned} 100A/4\pi R^2 &= 100\cdot\tfrac{1}{2}\operatorname{vers}\theta \\ &= 100\operatorname{havers}\theta. \end{aligned}$$

Haversines, like external secants, are not used generally, but tables of them are given in surveyors' and navigators' manuals. Also, the haversine being, like the external secant, essentially a cosine function, it becomes almost a straight line when graphed against a square root ordinate.

In the diagram as constructed, there is no line whatever for 6 months without sunshine, and the uppermost of the no-sunshine lines reaches the surface at 67° 26′, while the line for 6 months of constant sunshine reaches the surface almost a degree from the Pole. Similarly, while complementary lines meet neatly over the Pole itself, in lower latitudes the supplementary lines do not meet by 1° 30′ at the surface.

All these facts emphasize that, because of refraction, the actual sunshine conditions in polar regions deviate considerably from those postulated without considering refraction. Most geographers, and educated people generally, know that, despite popular jokes to the contrary, night does not last for six months everywhere in the polar regions. They have learned that only at the pole itself is there six months of constant sunshine, and six months without the sun, and that as distance from the pole increases, the length of the periods of constant sunshine and without sunshine decreases, with the intervals between having the more conventional alternation of night and day every 24 hours. But many geographers may be surprised to learn that the effect of refraction is to give the Pole approximately half a week more than 6 months with sunshine, half a week less without sunshine.

In latitudes 66° 33′ N. and S. geographers draw the Arctic and Antarctic Circles which, by definition, enclose the polar regions where, also by definition, the sun does not sink below the horizon at least once during the year and also does not rise above the horizon at least one day a year. But if the combined refraction and semidiameter correction is taken to be 53′, actually the sun is visible, for at least a few minutes, on every day of the year as far as 60 miles within the polar circles, and stays visible on the horizon at midnight on at least one day a year to a distance of 60 miles outside the circles. Thus the polar circles are quite fictitious, although the corresponding Tropics of Cancer and Capricorn are actually just what they're supposed to be: the boundaries of the region in which the center of the sun is directly overhead at noon at least once a year.

In constructing the diagram, sunlight intensity was not considered, and thus technically what are delimited are regions of the free atmosphere in which the sun is visible or invisible

for specified periods. To adapt the diagram for sunlight of any given intensity, changes must be made in R and in the declination correction.

If 65 km. (39 miles) is still taken as the effective height at which the earth's atmosphere refracts sunlight appreciably, it

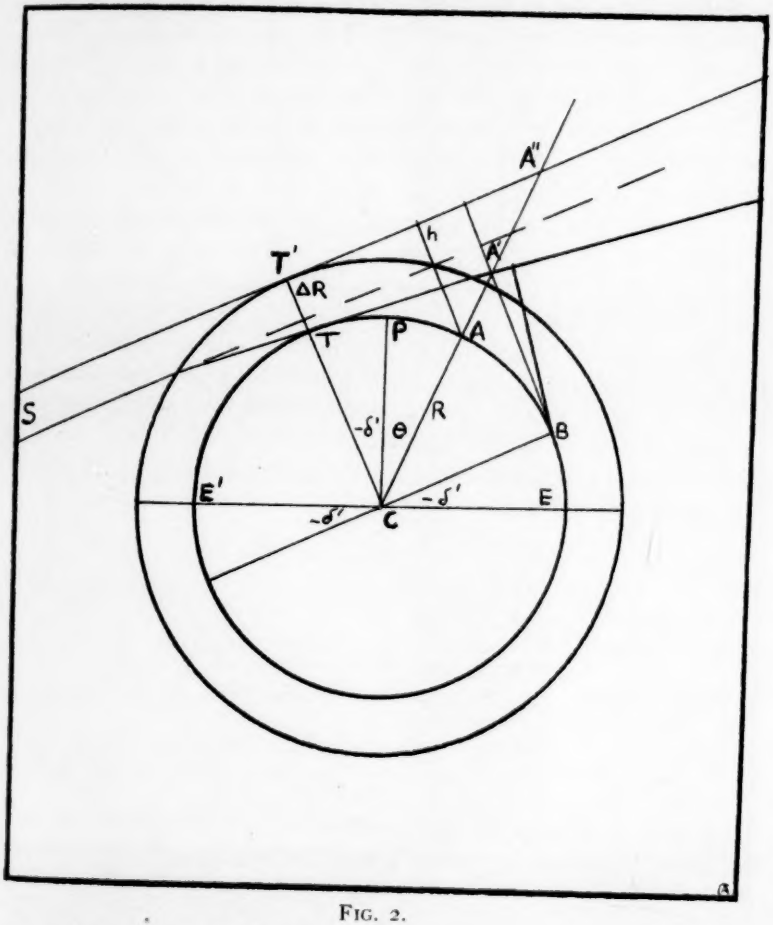

FIG. 2.

is also the height at which sunlight is undiminished by atmospheric absorption. In Fig. 2, the height AA'' of sunlight which has passed 65 km. above the surface and continued on, unrefracted, can be determined just as was the height h, and is

$$s' = (R + \Delta R) \sec (\theta - \delta') - R.$$

Since adding ΔR, the thickness of the refracting, absorbing layer, involves a total change of barely 1 per cent., a good approximation may be obtained by considering

$$s' = R \operatorname{exsec} (\theta - \delta'),$$

which is the same as the first formula for s except that δ' is the true solar declination, uncorrected for any refraction. In addition, 16′ for semidiameter may be *subtracted* from δ' to obtain the declination of the sun's lower limb, so that the result will refer to regions in which the entire solar disk is visible, undiminished by any appreciable absorption and virtually unaffected by refraction.

To graph the regions where this pure sunshine prevails, it is sufficient to use Fig. 3, moving all the curves to the right by 1° 46′ of latitude, and, of course, blocking out the entire portion below 65 km.

Study of the diagram, in the light of these explanations, should reveal many facts of interest to physicists in their studies of aurora and of ozone distribution and formation, and may conceivably be of benefit in the study of cosmic rays, as well as have a distinct bearing on the meteorology and climatology of polar regions.

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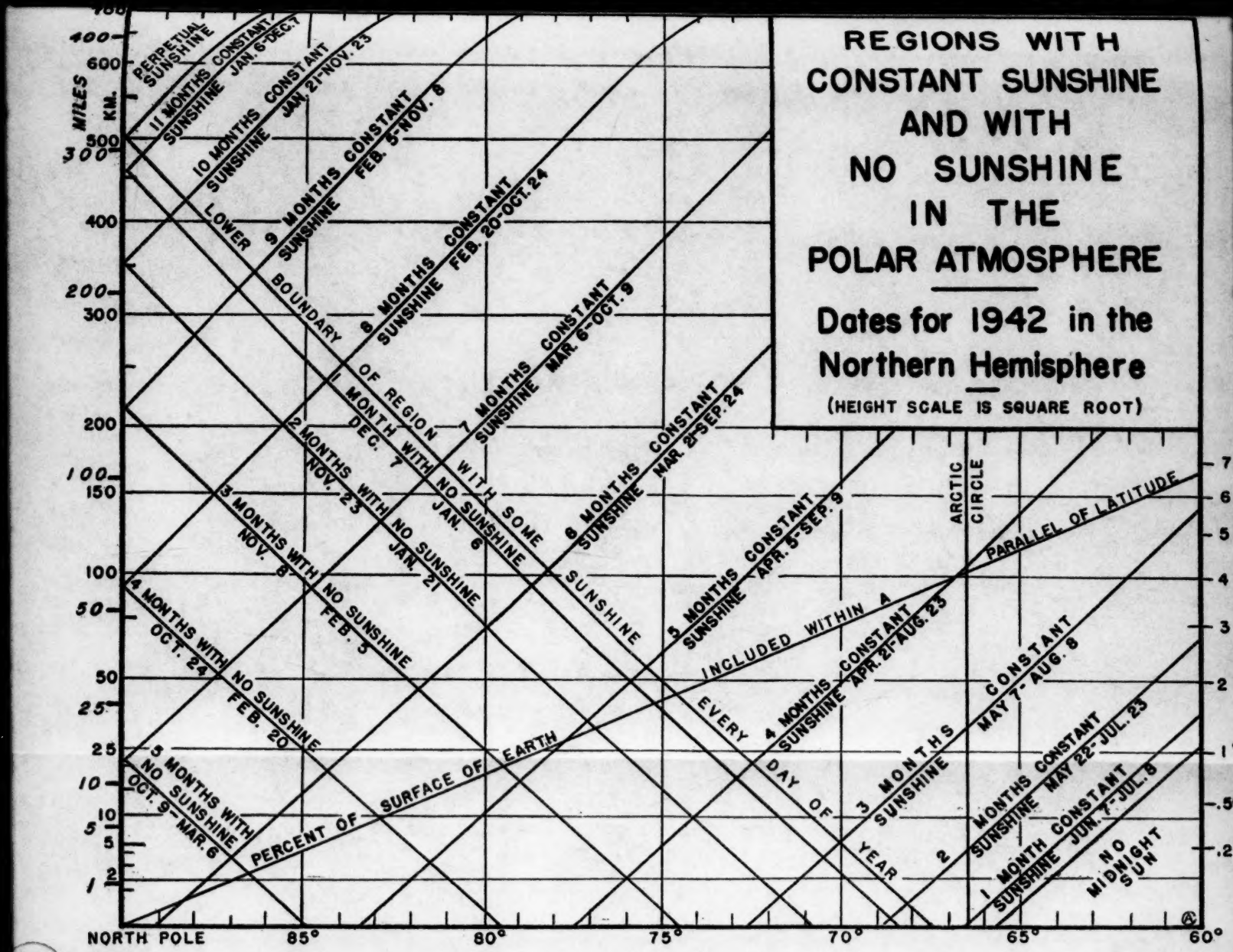
REGIONS WITH CONSTANT SUNSHINE AND WITH NO SUNSHINE IN THE POLAR ATMOSPHERE
Dates for 1942 in the Northern Hemisphere
(HEIGHT SCALE IS SQUARE ROOT)
MILES
KM.
PERPETUAL SUNSHINE
11 MONTHS CONSTANT SUNSHINE JAN. 6-DEC. 7
10 MONTHS CONSTANT SUNSHINE JAN. 21-NOV. 23
9 MONTHS CONSTANT SUNSHINE FEB. 5-NOV. 8
LOWER
8 MONTHS CONSTANT SUNSHINE FEB. 20-OCT. 24
BOUNDARY OF REGION
7 MONTHS CONSTANT SUNSHINE MAR. 6-OCT. 9
1 MONTH WITH NO SUNSHINE DEC. 7
2 MONTHS WITH NO SUNSHINE NOV. 23
3 MONTHS WITH NO SUNSHINE NOV. 8
4 MONTHS WITH NO SUNSHINE OCT. 24
5 MONTHS WITH NO SUNSHINE OCT. 9-MAR. 6
WITH SOME SUNSHINE
JAN. 6
JAN. 21
FEB. 5
FEB. 20
6 MONTHS CONSTANT SUNSHINE MAR. 21-SEP. 24
5 MONTHS CONSTANT SUNSHINE APR. 5-SEP. 9
4 MONTHS CONSTANT SUNSHINE APR. 21-AUG. 23
3 MONTHS CONSTANT SUNSHINE MAY 7-AUG. 8
2 MONTHS CONSTANT SUNSHINE MAY 22-JUL. 23
1 MONTH CONSTANT SUNSHINE JUN. 7-JUL. 8
NO MIDNIGHT SUN
ARCTIC CIRCLE
PARALLEL OF LATITUDE
INCLUDED WITHIN A
EVERY DAY OF YEAR
PERCENT OF SURFACE OF EARTH
NORTH POLE
85°
80°
75°
70°
65°
60°

FIG. 3.

POLAR ATMOSPHERE
IN THE
NO SUNSHINE
AND WITH
CONSTANT SUNSHINE
Data for 1942 in the
Northern Hemisphere

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

WAR TIME REVISION OF CODE FOR ELECTRICITY METERS.

For more than three decades the Code for Electricity Meters has been the generally recognized standard of practice in the art of metering electric energy. Originally issued in 1910 by the joint action of the Meter Committees of the National Electric Light Association and the Association of Edison Illuminating Companies, the Code has been revised from time to time, the latest extensive revision having been completed in May 1941 under ASA Sectional Committee procedure, with the Bureau, the Association of Edison Illuminating Companies, and the Edison Electric Institute as joint sponsors. The Code has formed a guide for the official regulations promulgated by the public utility commissions of many States, and in some States has been adopted in toto. One of the many practices recommended in the Code is a suggested schedule for the periodic testing and readjustment of watthour meters.

The flow of manpower to war industry and to the Army has left the utility meter departments with depleted staffs of skilled testers. Limitations on gasoline and rubber are further reducing the number of meters per day which a single tester can handle. It therefore appeared desirable, if it were technically advisable, to reduce the burden of meter testing by increasing the permissible interval between tests of the smaller sizes of meters, particularly those in residences, which constitute the great bulk of the meters in use.

At the suggestion of the EEI and the AEIC, the Sectional Committee C12 was constituted a War Standards Committee for this purpose and certain vacancies in its membership were filled. The question was first referred to a subcommittee consisting of F. E. Davis, Commonwealth and Southern Corporation; P. L. Holland, Public Utilities Commission of Maryland; R. H. Nexsen, Public Service Commission of New

* Communicated by the Director.

York; L. D. Price, Public Service Electric and Gas Company; A. R. Rutter, Westinghouse Electric and Manufacturing Company; and F. B. Silsbee, National Bureau of Standards, Chairman.

Fortunately, data were obtained by Mr. Price and from the records of the Department of Public Service, State of Washington, on the performance of several thousand meters over long periods of time. An examination of these data showed that the drift in calibration of the great majority of these meters had been very slight and that the number drifting fast was about offset by an equal number which became slow.

It was therefore decided, without dissenting vote in either the subcommittee or the main committee, that the interval between tests of a-c meters rated at 12 kilovolt amperes and less could be extended to 8 years without danger of doing an injustice to either the power companies or their customers. This revision was approved November 5, 1942, as an American War Standard. The official designation is C12 WS-1942. Copies of the revised section of the Code can be obtained from the American Standards Association, 29 West 39th Street, New York, N. Y.

ELECTRODE HOLDER FOR SPECTROGRAPHIC ANALYSIS.

The spectrographic analysis of metals, refractories, and other materials has replaced the older chemical methods in many cases, particularly in control or inspection testing. The advantages of the newer method are higher sensitivity of detection of metallic elements, improved precision, and greater speed. To realize the full potentialities of the spectrographic method, attention has been given to improving both the procedures and the design of equipment. One of the operations in this method, which not only involves time-consuming manipulation but also some danger to the operator, is the excitation of electrode samples. This operation involves volatilization of metallic vapors into the electric arc or the electric spark with potentials which may be as high as 40,000 volts. An electrode holder, designed by Bourdon F. Scribner and Charles H. Corliss and built in the Bureau's

shop, meets more rigid requirements of speed and safety in general spectrographic testing. As described and illustrated in the January Journal of Research (RP1515), the holder consists of water-cooled precision-acting copper clamps mounted on rigid ways and equipped with various controls designed for rapid and positive action. The controls are operated outside of a grounded safety housing which serves to protect the operator against harmful radiations, fumes, and electrical shock. The holder has proved useful in speeding-up a variety of spectrographic analyses of importance to the war effort and, at the same time, has afforded greater precision and safety.

ELEVATOR WIRE ROPE MAINTENANCE.

The maintenance of wire rope used for elevators, with special reference to war conditions, is discussed in Circular C441 which has just been released. This Circular was compiled by John A. Dickinson of the Bureau's safety codes' section and represents the views of the Executive Committee for the American Standard Safety Code for Elevators, Dumbwaiters, and Escalators. It covers the items affecting the life of wire rope, such as lack of lubrication, unequal tensions, misalignment of sheaves, inadequate maintenance of sheave grooving, poor brake setting, unduly high peaks of acceleration and retardation, and changes in top and bottom hoistway clearances. Methods of checking and correcting these particular items are discussed, and the publication closes with a suggestion that rope life be extended by decreasing elevator service either by running fewer cars or by establishing skip stops, or by similar methods.

Copies of C441 are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price is 5 cents.

THERMAL EXPANSION OF SOME BRONZES.

Results obtained in the course of independent tests and investigations on the linear thermal expansion of four groups

of copper base alloys designated as tin-zinc, leaded, aluminum and silicon bronzes, are tabulated in a paper by Peter Hidnert (RP1518) in the January number of the *Journal of Research*. Curves showing the typical expansion and contraction behavior of these bronzes during heating and cooling, are presented.

Ternary diagrams are given for the copper-tin-zinc and copper-tin-lead alloys to show the effect of composition on the coefficients of expansion. In general, the coefficients of expansion of these copper base alloys increase as the addition of tin, zinc or lead is increased.

Table 3 of the paper gives a summary of the coefficients of expansion of various bronzes for three temperature ranges. For the range from 20° to 100° C., the average coefficients of expansion were found to be between 16.8×10^{-6} and 19.0×10^{-6} per degree C. The maximum coefficient of expansion was found to be 64×10^{-6} per degree C. between 900° and 1000° C. for a silicon bronze.

FIRE RESISTANCE CLASSIFICATION OF BUILDING CONSTRUCTION.

One of the basic objects of public regulation of building construction is to secure reasonable safety from fire. Regulations relating to the construction and spacing of buildings are founded on long community experience with fire as a destructive agent. Many of the older cities and ruins of cities that are found today are underlaid by the ruins of still older cities, in the destruction of which fire played an important if not a sole part. Within comparatively recent times many cities have been practically leveled by fire, and such safety as now obtains has been achieved in considerable part as the result of this experience. Individual occupants of buildings are vitally interested, because fire can with startling suddenness, transform a friendly shelter into a place from which one must fly at the peril of one's life.

As the result of this experience with fires, a type of building has been developed which is generally designated as fireproof. It can withstand a complete burn-out of contents without collapse of structural members, although these, as well as

the building finish and trim, will be damaged in fires of any considerable intensity and duration. For buildings with the lighter amounts of combustible contents the spread of fire will be retarded and structural fire barriers can be provided that will generally confine even very severe fires within given areas. The hazard to neighboring construction from fires in such buildings is comparatively small, and they have often acted as barriers to the spread of conflagrations.

In Building Materials and Structures Report BMS92 on the fire resistance classification of building construction, it is assumed that "fireproof" buildings will be constructed in a considerable range of fire resistance appropriate to the hazard presented by their occupancy and contents. A method is given for evaluating the fire severity to which buildings may be subjected, in terms of the amount of combustibles which they contain. Greater economy and safety are thus made possible than would be the case if a fixed degree of fire resistance were required, too high for low-hazard occupancies of residential type, and insufficient to withstand the severe fires that can occur in mercantile, factory, and storage buildings. The recommendations are supplemented with data on fire-resistance ratings of floors, walls, columns, and other members, which afford a considerable range in choice of constructions that will withstand a given fire severity.

The second type of construction defined in BMS92 has incombustible interior and exterior construction. Its fire resistance is limited to ability to withstand a severe fire for ¾ hour. With light-hazard occupancies, no collapse of structural members is likely to occur even if fires are not extinguished, and the same holds for potentially severe fires controlled in their early stages. Where collapse occurs it would be likely to pull the exterior walls toward the inside, and the incombustible floor and roof would tend to blanket the fire.

The third type, termed exterior-protected, comprises buildings with exterior masonry walls and interior wood construction. The outside walls with protected openings are effective in preventing spread of fire from building to building for all but very severe exposures. In common with the preceding

type, the interior construction can, without much difficulty, be made to have a fire-resistance rating of ¾ hour, although as for the other type, buildings with lower fire resistance are recognized as coming within the group. This type of building has served acceptably in preventing sweeping conflagrations where the general size of buildings involved and amount of combustible contents were not too large.

The remaining type includes buildings with wood exterior and interior construction. As with the two preceding types, the fire resistance of their structural members can be increased till it is appreciably above that of unprotected members. Incombustible veneers that can be applied to outside walls, will give resistance to exterior fire exposure approaching that of exterior-protected type of construction.

The bases for restrictions and limitations are outlined from the standpoint of fire zoning, height and area of building, distance from lot line or adjacent building, permissible materials and occupancies, and required degree of fire resistance, and are discussed in their relation to the different types of construction. No definite recommendations are made concerning these particulars. They can best be settled for each municipality after considering local conditions. The report includes a summary of such restrictions and limitations, as they are applied in six typical building codes.

Copies of BMS92 are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price is 25 cents.

MOISTURE IN WALLS OF FRAME HOUSES.

The widespread application of air conditioning to houses to promote better health and comfort has brought a problem in building construction. Vapor from the warm, humidified inside air enters the walls and often accumulates there during cold weather to an extent that may cause serious damage. The Bureau has studied the problem in coöperation with the Insulation Board Institute, by actually observing what took place inside the north wall of a frame house during winter weather while a relatively high humidity was maintained

inside the house. Seven different constructions were exposed simultaneously as adjacent full-height sections of the wall.

As explained in Building Materials and Structures Report BMS93, copies of which are now obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 10 cents each, condensation within walls can be avoided by using a vapor barrier to prevent the moisture from entering the walls from the warm side. In instances where this type of protection was not employed, condensation occurred during an exposure of 2 weeks duration in Washington, D. C., during moderate winter weather. There was no basic difference between the performance, with respect to the accumulation of moisture, of walls of standard wood construction and those in which fiber sheathing boards were used. In all instances of condensation, the accumulation of moisture was greatest in the lower portions at or near the sills where decay would be a serious matter.

PAINTS AND OTHER PROTECTIVE COATINGS FOR TIRES.

Letter Circular LC709, released last month, answers questions frequently received by the Bureau concerning tire paints.

These paints and other protective coatings may serve to improve the appearance of tires and to protect the rubber from cracking and checking caused by sunlight and weather, but no products are known that will restore or rejuvenate old rubber, or increase the mileage of treads.

Materials offered for use on tires can be tested by applying them to alternate sectors of tires and comparing the treated and untreated areas after a reasonable mileage. A product to be worth testing on the road should form a waterproof, adherent film, or should be absorbed by rubber.

It is recommended that tires having white sidewalls and the tires of unused vehicles exposed to the weather be painted for protection. When protection is needed against radial cracks or severe checking of the sidewalls a solution of an antioxidant and a sun-checking inhibitor should be applied. The large majority of tires, however, require no treatment beyond intelligent care and maintenance.

MECHANICAL PROPERTIES OF CELLULOSE ACETATE.

Textile fibers must meet certain specifications as to mechanical properties, such as strength, flexibility, or resiliency. The more important fibers owe their individual successes to the possession, to a greater or less extent, of certain of these desirable characteristics. It has been shown by many investigators that these properties are related to the length, arrangement, and chemical nature of the chain-like molecules of which the fibers are composed. The investigation reported in RP1513 (January *Journal of Research*) by Arnold Sookne and Milton Harris, Research Associates of the Textile Foundation, is concerned with only the first of these factors, namely, the influence of the length of molecules. The material used was cellulose acetate which had been carefully fractionated with respect to molecular chain-length. The average length of the chains in the fraction containing the longest molecules was roughly ten times that of the chains in the fraction containing the shortest.

It was found that the fraction of lowest chain-length would not form a coherent film; fractions of longer chain-length formed films which showed rapid improvement in mechanical properties with increasing chain length; however, with the fractions of greatest chain-length, further improvement was only slight. When blends of the fractions were investigated, it was found that inclusion of fractions of shorter chain-lengths exerted a harmful effect on the mechanical properties of the films. This is consistent with the concept that structures of such materials fail when a sufficient number of chain ends appear close together. Obviously, the number of ends in any cross-section of a sample increases as the average chain-length decreases.

PHOTOCHEMICAL STABILITY OF PAPERS.

Light has an important effect on papers. The conditions under which exposure takes place usually involve room temperatures and sky light transmitted by glass windows. To simulate these conditions, while studying the photochemical stability of papers, Herbert F. Launer and William K. Wilson

used a powerful light source provided with a special filter to remove the objectionable portions of the ultraviolet and infrared ends of the spectrum. During irradiation the papers were maintained near 30° C. and a normal humidity. Thus, the heat effects which have been shown to overshadow light effects under ordinary experimental and testing conditions involving high intensity sources, were eliminated.

As shown in the Journal of Research for January (RP1517), the results obtained differ considerably from those of previous workers. The yellowing of papers (containing little or no lignin) commonly ascribed to light was found to be a result of heat effects or age, but not of light; when heat effects were eliminated during irradiation, all the papers were bleached by light. Even highly lignified paper, such as newsprint, was bleached by light in the absence of oxygen.

Paper scorched brown at high temperatures or yellowed at 100° C., and papers 250 years old and very yellow, were bleached by light in the absence of heat effects.

It was found that lack of oxygen inhibits photochemical deterioration, but does not prevent it altogether. Lack of water vapor decreased the rate of alpha cellulose change in papers made from wood pulps, but increased the rate in those derived from cotton. The rate was found to be proportional to less than the first power of time of irradiation and of light intensity.

Under normal conditions the order of the photochemical stability of papers made from various kinds of fibers was as follows, starting with the most stable: New cotton rag, refined sulfite, old cotton rag, soda-sulfite mixtures, and newsprint. The stability of new rag papers was greatly affected by acid and rosin, whereas that of old rag and soda-sulfite was only slightly affected. This is in marked contrast to heat stability, for which the pH is important for all fibers. Newsprint, made neutral with $NaHCO_3$, showed a large increase in light stability. Rosin did not seriously affect the light stability of new rag papers, as long as the acidity was low. Little difference between ordinary rosin and hydrogenated rosin was found in this connection. Any effect of glue and starch sizing could be ascribed to the acid of the sizing bath. Fillers had no significant effect.

Lignin was found to render paper very unstable to light, and was itself converted to acid substances, the acidic nature of which probably plays no direct part in the photochemical deterioration. Lignin had a greatly diminished effect at low concentrations of oxygen.

Certain dyes were found to increase deterioration by light. Printers' ink extensively protected the paper beneath it.

Papers once irradiated were found to be subsequently less stable in the dark than those not previously irradiated.

THE FRANKLIN INSTITUTE.

ANNUAL MEETING, JANUARY 20, 1943.

At 8:15 P.M. on Wednesday, January 20, 1943, the annual meeting of The Franklin Institute was called to order by Mr. Charles S. Redding, President.

The National Anthem was played on the Hammond organ, an instrument used by the lecturer to demonstrate a portion of his lecture.

Mr. Redding announced that the minutes of the previous meeting had been printed in full in the January number of the JOURNAL OF THE FRANKLIN INSTITUTE and that, unless objection were offered, they would be approved as printed. Upon motion they were declared approved.

The President then called upon the Secretary of the Institute, Dr. Henry Butler Allen, who reported that since the last meeting the following additions to membership had been made:

Sustaining	2
Active	113
Associate	30
Student	51
Total	196

The Secretary then read the report of the Tellers of the annual election, which follows:

President (to serve one year)	Charles S. Redding
Vice-Presidents (to serve one year)	Walton Forstall
	W. Chattin Wetherill
	S. S. Fels
	Richard W. Lloyd
	Richard T. Nalle
Treasurer (to serve one year)	Morton M. Price
Managers (to serve three years)	Irenee duPont
	W. H. Fulweiler
	Nathan Hayward
	Horace P. Liversidge
	Malcolm Lloyd, Jr.
	Marshall S. Morgan
	Edward Warwick
	D. Robert Yarnall
(to serve two years)	Hiram S. Lukens
(to serve one year)	James H. Robins

Respectfully submitted,

GEORGE S. CRAMPTON,
GEORGE S. CULLEN,
J. LOGAN FITTS,
Tellers.

The gentlemen named were then declared elected to their various positions for the time indicated.

With the approval of the Board of Managers, the Secretary then submitted the name of Carl Van Doren for Honorary Membership in The Franklin Institute, "In consideration of his researches and contributions to the literature of our times, whereby the life of Benjamin Franklin is being reincarnated for all peoples of the present, bringing courage and confidence that such heritage shall not be lost."

Upon motion, duly seconded and carried, Dr. Van Doren was elected an Honorary Member.

The President expressed appreciation to the Tellers for the service they had endered in counting and tabulating an unusually large number of votes.

Mr. Redding then reminded the members that his report as President to the Board of Managers was usually presented at this annual meeting. He stated that it had been received by the Board in the afternoon and would be printed in full in the JOURNAL. He then briefly outlined important features, such as source of revenue, major activities, etc. and referred his listeners to the JOURNAL for full details.

Upon motion, the report of the President was approved and accepted.

The speaker of the evening, Dr. Abraham Pepinsky, Professor of Music Education, University of Minnesota, was then introduced. Mr. Redding gave an interesting account of former activities of the lecturer and then turned the meeting over to him. Dr. Pepinsky spoke on "Contributions of Science to an Appreciation of Music." He pointed out that a physicist's objective measurement of musical phenomena is treated by the psychologist for its subjective effects on the human organism and stated that musical understanding, arising from such scientific contributions, tends to broaden the appreciation of music for the creator and performer as well as the listener. The lecturer used slides to illustrate his talk and was assisted in his demonstrations by selections played on the Hammond organ, and by Dr. W. F. G. Swann, Director of the Bartol Research Foundation of The Franklin Institute, who performed on the cello.

A discussion followed the talk. The meeting was dismissed by a rising vote of thanks to the lecturer, at ten-thirty P.M.

HENRY BUTLER ALLEN,
Secretary.

January 19, 1943.

Report of the President to the Board of Managers of The Franklin Institute of Pennsylvania, Covering the Operations of the Institute for the Year 1942.

Our By-Laws provide that at the Annual Meeting of the Institute, the Board of Managers shall through its President, present a report of the affairs of the Institute. The following report by the President was today approved by the Board and the President was instructed to present it at this meeting as the report of the Board.

* * *

This report is a brief summary of the financial operation and of the activities of The Franklin Institute for the year 1942.

The property of the Institute is entered on its books at $5,675,500. Of this amount, real property (the building and equipment, not including those exhibits which have been donated) amounts to $4,108,000, and personal property (principally securities as referred to later) and cash amount to $1,567,500.

Not entered in its books, except statistically, is certain other property consisting of exhibits, etc., which came to the Institute as gifts.

The following figures, covering income and expense and deficit, are subject to minor adjustments after the books are closed.

Income for 1942 consisted of the following, set forth comparatively with 1941 figures:

	1942	1941
From dues	$ 30,200	$ 22,700
" admissions	38,200	42,600
" investments	69,100	74,300
" other sources	178,200 *	48,600
" Friends of Franklin	26,400	35,150 †
	$342,100	$223,350

Expenses for 1942, with the same comparison, were as follows:

	1942	1941
General	$156,900	$140,000
Museum Operation	85,000	95,000
Publications	11,000	11,600
Meetings, etc.	1,800	1,800
National Franklin Committee	18,800	0
Other	100,500 ‡	18,500
	$374,000	$266,900

The deficit for 1942 was, therefore, $31,900, as compared with $43,550 in 1941. In order, however, to make a more fair comparison with the results of 1941, the expenses of the National Franklin Committee, in 1942, which committee will be later commented upon, should be deducted, resulting in a deficit of $13,100. This improvement over last year's operation is largely due to work being done at the Institute in connection with our country's war activities, later referred to, and for which the Institute is being compensated.

At the end of 1942 the Institute's investments in securities were:

Largely available as to income only	$ 579,800
Available unrestrictedly	978,700
	$1,558,500

The membership, all classes, was 4,677 at the end of the year, a gain of 1,294 as compared to 1941.

Admissions to the Museum and Planetarium with comparable figures for 1941, were as follows:

---

* Includes amounts paid by and due from government agencies for war work.

† In last year's report Friends of Franklin contributions were shown net after allocation of expense of solicitation. In this report the amount of contributions is shown as gross amount collected for each year.

‡ This figure includes approximately $85,000 applied to carrying on war work.

	Museum		*Planetarium*		*Total*	
	1942	1941	1942	1941	1942	1941
Paid at 25¢ rate	89,838	84,206	44,417	52,678	134,255	136,884
Paid at various special rates	18,457	32,036	13,547	27,626	32,004	59,662
Free, Phila. School Children	13,234	25,974	7,618	10,308	20,852	36,282
Free, Members and Others	14,033	9,712	11,610	8,518	25,643	18,230
	135,562	151,928	77,192	99,130	212,754	251,058

During the year 14 Institute lectures were held. Altogether there were 547 meetings of various kinds at the Institute.

Your officers and managers have been much gratified and heartened by the generous financial assistance of Friends of Franklin. In the above income statement it will be noted that $26,400 was contributed by that group making it possible to continue activities which otherwise would have had to be further curtailed or eliminated.

During the year a large part of the time of our technical staff and added personnel, under the direction of Dr. Allen, has been devoted to research and development work connected with the war effort and the Institute has been complimented by various government agencies for the results accomplished. This type of work will be continued in 1943 at perhaps an accelerated pace. The Institute has been compensated for this work at cost with the result that a portion of our salary roll and overhead expenses ordinarily chargeable to Operations, have been offset by payments received from government agencies, thus largely accounting for the decrease in Operating Deficit previously referred to. It is quite proper and fitting that The Franklin Institute should engage in such activities during this crisis in our Country's history, the sixth war in the life of the Institute.

Despite the fact that our technical staff has been largely engaged in war work, the Museum and Planetarium have carried on in excellent shape. During the year, there was developed a fine exhibit on camouflage for National Defense. A lecture-demonstration was developed on the science of fire-fighting, which was given approximately 90 times and attended by approximately 17,000 people, including all members of the Police and Fire Departments of the City of Philadelphia. There was also developed an exhibit covering Air Raid Precautions for the Home.

We have presented three special Planetarium demonstrations during 1942, one of them sponsored by the Westinghouse Electric & Manufacturing Company.

Certain very important exhibits, including the prized Frankliniana, have been placed in safe storage for the duration.

The Institute Lecture Hall has been designated as a Public Air Raid Shelter.

Ninety-one companies have accepted our request for industrial coöperation, including fourteen companies which have contributed toward the building of a steel castings exhibit to be opened in a few months. Practically 100 per cent. of those which accepted industrial coöperation have renewed, and upon our third request for renewal to date, all have accepted, which indicates industry has shown an interest in our program. In accepting financial responsibility they are taking more interest in their exhibits.

The courses in Navigation and Meteorology, in which our Planetarium is used, given at the Institute by the Air-Mar Navigation Schools, have been extremely popular.

These are just a few of the activities of the Museum and Planetarium during the year and are mentioned to indicate clearly that the staff has been earnestly endeavoring to adapt itself to current war needs.

The Library has been increasingly used in connection with the War. During the year 8,346 individuals consulted it in person, and 3,614 by telephone; approximately 5,000 books were taken out and approximately 4,000 photostats were furnished. These figures show an increase over those of last year.

Much credit is due the Membership Committee and the members of the staff engaged in membership activities for the fine work done during the year. In December, in charge of the Membership Sales Department, a new project was instituted, to secure additional advertisements for the JOURNAL OF THE FRANKLIN INSTITUTE.

The other committees of the Institute have carried on their work during the year and every effort has been made in spite of the War to continue The Franklin Institute in all its aspects as a vital influence in our community and the nation.

The Hostess Committee has been particularly active and much credit is due that group for what it has accomplished. Recreation and rest rooms have been newly furnished. The Dairy Dell has been improved. The Committee has furnished an outdoor lounge for use during warm weather and, in addition, has paid into the Institute's treasury $400.00 for such use as the Institute might care to make of that sum. On the occasion of the Medal Day Dinner, the Committee arranged a very much appreciated reception for President and Mrs. Redding.

The two Research Foundations, Bartol and Biochemical, have devoted practically all of their energies to work pertinent to various government agencies in connection with the Nation's war activities. Their Directors made Annual Reports at Stated Meetings of the Institute, but due to the confidential nature of much of the work carried on during the year, were not in a position to report fully upon the accomplishments of the Foundations. Financial statements of the two Foundations are not included in this Report for the reason that each has its own funds disassociated from those of the Institute and not contributed to by the latter.

On December 31, the organization comprised the following employees, including salaried and non-salaried:

The Franklin Institute	166
Bartol Research Foundation	32
Biochemical Research Foundation	52
	250

Starting in the latter part of 1941, there was established a committee now known as the National Franklin Committee, under the chairmanship of Mr. William Vermilye, of New York, the purposes of which are to nationalize and vitalize the virtues and teachings of Benjamin Franklin, to make The Franklin Institute and its varied activities better known throughout the country, and eventually, to widen the scope of support of the Institute. This Committee with the consent and approval of the Board of Managers was fortunate in securing the aid of Mr. Edward L. Bernays, a nationally known authority on publicity,

to assist in carrying on this work. The results of this venture will probably not be apparent for several years to come, but it is hoped that, through it, means will be found, eventually, not only to carry on our present activities without annual deficits, but to increase those activities.

The following gentlemen were elected by the Board of Managers to fill existing Board vacancies:

Mr. J. H. Robins, President of The American Pulley Company,
Dr. Hiram S. Lukens, Director, Department of Chemistry and Chemical Engineering, University of Pennsylvania,
Mr. D. Robert Yarnall, President of Yarnall-Waring Company,
Mr. Wilson S. Yerger, President of Imperial Type Metal Company.

It was with regret that the Board accepted during the year the resignation of Mr. William Fulton Kurtz as a member of the Board. Mr. Kurtz found that his many activities made it impossible for him to continue membership on the Board.

During the year the Board of Managers suffered the loss due to death of Mr. Clarence A. Hall, who was elected a member of the Board in 1922 and who faithfully served the Institute in various capacities up to the time of his death.

Within a few days after Mr. Yerger was elected to the Board, he died suddenly. Mr. Yerger had been a member of the Institute for many years, was very much interested in its progress, was a liberal contributor to the Institute through Friends of Franklin, and the Board had looked forward to his more active participation in the Institute's affairs.

Recently the Institute was informed of a legacy in a substantial amount left by Dr. William L. C. Eglin, who was President of the Institute from 1924 to 1928. This will shortly become available. Also, upon the death of a sister of Dr. Eglin, there came to the Institute a portrait of Dr. Eglin which has been placed upon the walls of the Institute.

In the latter part of December we were informed of a bequest of $500 which will be received shortly from the estate of Charles McDowell.

It is a tribute to The Franklin Institute and to Dr. Allen that during the year he was sent by the Government upon a mission to England in connection with our war activities.

The men and women of the Institute's organization have rendered earnest and effective service during 1942 despite continued handicaps, chief among which is the limitation of our income. It is still necessary to control expenses and to be constantly on the alert in order to keep our deficit at a minimum. The organization is well aware of this situation, however, and still carries on with high spirit. I express my sincere personal appreciation to the executives and staff for the fine work which has been accomplished.

At the end of this, my first full year as President, I express also to the officers and to the members of the Board of Managers my deep appreciation of their friendly and helpful assistance in endeavoring to perpetuate the ideals and objectives of The Franklin Institute.

CHARLES S. REDDING,
President.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, January 13, 1943.)

HALL OF THE COMMITTEE,
PHILADELPHIA, JANUARY 13, 1943.

MR. JOHN B. KLUMPP *in the Chair.*

The following reports were presented for final action:

No. 3117: Henderson Medal.

This report recommended the award of a George. R. Henderson Medal to HARRY MILLER PFLAGER, of St. Louis, Missouri, "In consideration of his outstanding engineering achievements as a pioneer in the design and development of large integral castings, contributing in part to the use of high capacity modern power units and resulting in reduced operation costs."

No. 3118: Brown Medal.

This report recommended the posthumous award of a Frank P. Brown Medal to ALBERT KAHN, of Detroit, Michigan, "In recognition of his outstanding achievements in the development of industrial architecture."

No. 3119 } The Standing Sub-Committee on the Franklin Medal recom-
No. 3120 } mended that a Franklin Medal be awarded in 1943 to:

GEORGE WASHINGTON PIERCE, of Cambridge, Massachusetts, "In recognition of his outstanding inventions, his theoretical and experimental contributions in the field of electrical communication, and his inspiring influence as a great teacher"; and one to

HAROLD CLAYTON UREY, of New York, New York, "In recognition of his discovery of an isotope of hydrogen of mass 2 which has resulted in the opening of new fields of knowledge in three of the physical sciences."

JOHN FRAZER,
Secretary to Committee

LIBRARY NOTES.

The Committee on Library desires to add to the collections any technical works that members would wish to contribute. Contributions will be gratefully acknowledged and placed in the library. Duplicates received will be transferred to other libraries as gifts of the donor.

Photostat prints of any material in the collections can be supplied on request. The average cost for a print 9 × 14 inches is thirty-five cents.

The library and reading room are open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays from two until ten o'clock P.M.

RECENT ADDITIONS.

ASTRONOMY.

DERHAM, W. Astro-Theology. 1715.
SCOTT, ORAL E. The Stars in Myth and Fact. 1942.
WILLIAMS, KENNETH P. The Calculation of the Orbits of Asteroids and Comets. 1934.

AUTOMOTIVE ENGINEERING.

POLSON, J. A. Internal Combustion Engines. Second Edition. 1942.

BIOGRAPHY.

RUKEYSER, MURIEL. Willard Gibbs. 1942.

CHEMISTRY AND CHEMICAL TECHNOLOGY.

CHERONIS, NICHOLAS D. Semimicro and Macro Organic Chemistry. 1942.
FRENCH, SIDNEY J. The Drama of Chemistry. 1937.

ELECTRICITY AND ELECTRICAL ENGINEERING.

HUND, AUGUST. Frequency Modulation. 1942.
Radio Handbook. Ninth Edition. 1942.

MATHEMATICS.

FRANCOEUR, L.-B. Cours Complet de Mathématiques Pures. Cinquième Édition. Tomes 1–2. 1838.
GARDNER, MURRAY F., AND JOHN L. BARNES. Transients in Linear Systems. Volume 1. 1942.
MOORE, JUSTIN H., AND JULIA A. MIRA. The Gist of Mathematics. 1942.

METEOROLOGY.

HUMPHREYS, W. J. Ways of the Weather. 1942.
VETTER, ERNEST G. Visibility Unlimited. 1942.

MILITARY ART AND SCIENCE.

U. S. Selective Service System. Selective Service in Peacetime. 1942.

MINING AND METALLURGY.

BATEMAN, ALAN M. Economic Mineral Deposits. 1942.
BRAY, JOHN L. Ferrous Production Metallurgy. 1942.
The Mineral Industry during 1941. Volume 50. 1942.

NAVAL ART AND SCIENCE.

Excerpts from the International Code of Signals. 1942.
RICHARDS, PHIL, AND JOHN L. BANIGAN. How to Abandon Ship. 1942.
WOODBURY, DAVID O. What the Citizen Should Know About Submarine Warfare. 1942.

PHOTOGRAPHY.

American Annual of Photography 1943. Volume 57. 1942.
MEES, C. E. KENNETH. The Theory of the Photographic Process. 1942.

PHYSICS.

TOLANSKY, S. Introduction to Atomic Physics. 1942.
University of Pennsylvania. Bicentennial Conference. Fluid Mechanics and Statistical Methods in Engineering. 1941.

RAILROAD ENGINEERING.

HENRY, ROBERT SELPH. This Fascinating Railroad Business. 1942.

NOTES FROM THE BIOCHEMICAL RESEARCH FOUNDATION.

Experimental Burns: The Influence of a Gelatin-Glucose-Salts Solution on the Hemoconcentration of Burns.—J. O. ELY and A. W. ANGULO. In burns the greatest danger is shock and its associated disturbances which are the main causes of death. The local treatment of the burned area is of great importance, but of even greater importance in severe burns is the treatment designed to alleviate the physical and organic disturbances associated with shock. These disturbances often occur over a period of time after the burn injury.

Hemoconcentration, which may be considered a criterion of the resulting disturbances of burns, is the increased concentration of erythrocytes in the circulating blood resulting from a loss of fluid from the blood into the injured area. The hemoconcentration can be easily and accurately measured by hematocrit readings, specific gravity of the blood, the hemoglobin content, or the erythrocyte count. Moon who has had wide experience states ("Shock and Related Phenomena," V. H. Moon, Oxford University Press, 1938, p. 380) that he has found the erythrocyte count to be the most accurate of the four methods.

The loss of fluid from the blood into the burn-injured area, and the resulting hemoconcentration, vary with the extent and severity of the injury. The loss of fluid may be so great as to deplete to a critical point the volume of the circulating blood. The disparity between the volume of the circulating blood and the total volume-capacity of the circulatory system, if not compensated, causes circulatory deficiency.

It is generally recognized that in shock the volume of the circulating fluid should be restored to normal as quickly, and maintained as nearly normal, as possible. For this purpose the intravenous infusion of homologous serum or plasma is recognized, at present, as the most satisfactory. Other fluids have been used for this purpose with varying degrees of success. The intravenous administration of solutions of glu-

cose and of sodium chloride apparently offers only temporary relief because of the rapid loss of the solute from the circulating blood. Various fluids, containing non-diffusible solutes such as gum acacia, bovine serum albumin, hemoglobin and gelatin, have been, or are being, tried. The value and harmlessness of most of these fluids are not well established at present.

Hogan reported in 1915 ("The Intravenous Use of Colloidal Gelatin Solutions in Shock," James J. Hogan, *Journal of the American Medical Association*, **114**: 721) on the use of a gelatin solution for shock treatment. The solution which he used contained 2.27 per cent. gelatin, 0.95 per cent. sodium chloride, and 0.18 per cent. sodium carbonate ($Na_2CO_3.10H_2O$). The beneficial effects of the use of this solution in a case of severe traumatic shock, and in restoring the blood pressure in a number of other cases were reported as being very satisfactory.

Bayliss ("Intravenous Injections in Wound Shock," William Maddock Bayliss, Longmans, Green and Co., London, New York, 1918, p. 78) criticized adversely the use of gelatin solution to restore blood volume and advocated the use of gum acacia instead, stating that "fortunately gelatin has no properties of importance for our purpose that gum does not possess. . . ."

A gelatin-glucose-salts solution was prepared for this experiment and compared with serum in combating the hemoconcentration of experimental burns in rabbits. The results of the use of this solution are practically identical with those obtained with serum.

EXPERIMENTAL.

Rabbits of the New Zealand white breed averaging approximately 2 kg. in weight were used. They were maintained on Purina Rabbit pellets and had access to water. They were not fasted prior to the experiments. All blood samples were taken from ear veins. The hair from the back of each animal was clipped closely on the day prior to the experiment. On the day of the experiment an erythrocyte count was made as a standard. Evipal in a 14 per cent. solution in distilled water was then injected intravenously

until complete anæsthesia was obtained. (Evipal was chosen as an anæsthetic for two reasons: (1) The period of anæsthesia is brief in comparison to that produced by sodium amytal. (2) It appeared to have a negligible effect upon the erythrocyte count.) The dehaired back of the animal was then dipped into water at 94° C. for 8 seconds.

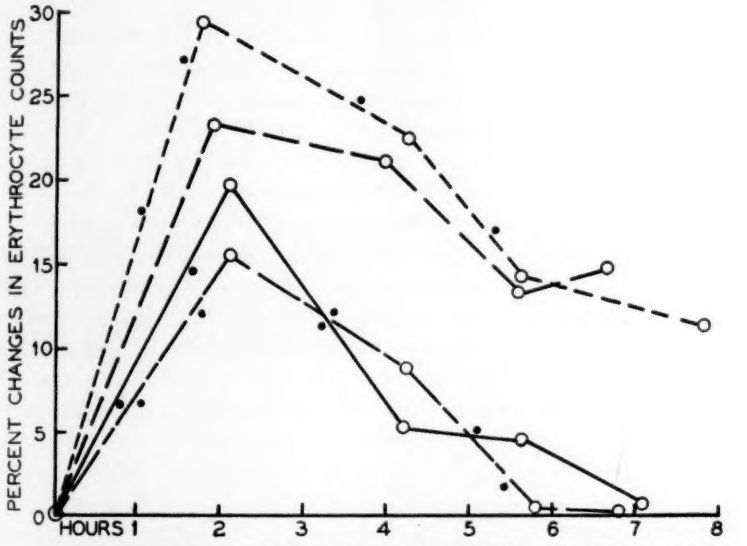

FIG. I EFFECT OF INTRAVENOUS INJECTIONS OF SERUM, 0.85% SODIUM CHLORIDE SOLUTION, AND GGS SOLUTION ON THE HEMOCONCENTRATION OF BURNS.

— — CONTROLS
—•— TREATED WITH RABBIT SERUM
——— TREATED WITH GGS SOLUTION
– – – TREATED WITH 0.85% SODIUM CHLORIDE SOLUTION
• INDICATES THE TIME OF INJECTIONS

The burns inflicted were approximately uniform. The temperature of the water and the time of immersion were kept constant but it was not feasible to control the depth of immersion well enough to produce burns of the same size in relation to the total body surface. However, measurements of the area burned and of the total body surface were made for

each experimental animal. The burn was traced on transparent paper and the burn-area determined by means of a planimeter. To compute the total body surface, the body of the animal was considered to be cylindrical. The height of the cylinder was the crown-rump-length and the volume was obtained by water displacement. The total body area was then determined. From these values the percentage of the total body surface burned was calculated.

Variations in the thickness of the skin of the animals also may have contributed somewhat to non-uniformity of the burns. When the rabbits were killed, at periods from 1 day to 2 weeks after inflicting the burns, it was difficult in some cases to classify the burns as to degree of severity. However, muscle injury beneath the skin indicated rather severe burns.

After inflicting the burns on the rabbits four additional erythrocyte counts were made during the following six hours. These counts were used as a measure of the hemoconcentration occurring after infliction of the burns. Four intravenous injections of 15 cc. each were made into ear veins of the rabbits treated with solutions for the control of the hemoconcentration. The spacing of these injections was approximately, but not identically, the same in each case. The average spacing in relation to the time of the erythrocyte counts is shown in Fig. I. The number of rabbits in each group and the percentage of the total body surface burned are shown in Table I.

TABLE I.

The Percentage of the Total Body Surface Burned.

	No. of Rabbits	Minimum	Maximum	Average
Group I: Controls	24	18.0	38.0	28.4
Group II: Serum treated	10	22.3	41.0	31.0
Group III: GGS Solution treated	26	20.0	37.0	29.2
Group IV: 0.85% NaCl treated	5	28.6	35.0	32.1

The serum used was obtained from the blood of rabbits of the same breed and was stored in a household refrigerator prior to use.

The composition and preparation of the solution designated GGS (Glucose-Gelatin-Salts) was as follows:

	Constituents	Grams
Sol'n 1.	Gelatin, Baker's U.S.P.	5.400
	Cysteine.HCl	0.018
	Phenol Red	0.010
	Sodium Chloride	1.440
	Potassium Chloride	0.036
	Calcium Chloride (anhydrous)	0.036
	Magnesium Chloride.$6H_2O$	0.018
	Sodium di-hydrogen phosphate	0.009
	Distilled water 100 cc.	
Sol'n 2.	Glucose	6.000
	Distilled water 100 cc.	

Solution 1 was sterilized by placing it in an autoclave for 30 minutes at 20 lbs. steam pressure.

Solution 2 was sterilized by passing it through a Seitz sterilization filter pad.

The two solutions were then mixed and designated GGS.

Toxicity Tests of GGS.—Gross pathological examinations of the organs of the burned animals and microscopic examination of the organs have not shown any pathological effect of the injections of GGS. Nearly all of the rabbits used showed pathological conditions but the lesions were not confined to any group.

In order to study the effect of the intravenous injections of GGS, uncomplicated by burns or anæsthesia, and in the frequency of injections used in the burn experiments, 5 rabbits were similarly injected and the results of the pathological examinations compared with those of 5 uninjected rabbits. No pathological findings could be attributed to the injections of the solution.

Because most of our so-called normal rabbits show pathological conditions, it is difficult to be certain whether such conditions existed previous to, or were produced by, the experimental procedure. For this reason GGS was tested for pathological producing possibilities by intravenous injection into growing rats.

In one experiment, two groups of female albino rats were used. They were selected so that their weights were approximately the same, the total initial weights of the two groups differing by only 0.4 grams. They were maintained on the laboratory stock diet and given access to water at all times. Intravenous injections of 2 cc. amounts of GGS were made into one group as shown in Fig. II, once a day, except on the

15th day when 2 injections of 3 cc. each were made. The other group was given, at the same time, and in the same amounts, injections of 0.85 per cent. sodium chloride solution. The growth curves of these two groups are shown in Fig. II.

Rats in Group II, injected with GGS, consumed 2.7 per cent. less feed and gained 9.3 per cent. more weight than did those in Group I which were injected with the saline solution. Fig. II shows the growth increase data in graphic form.

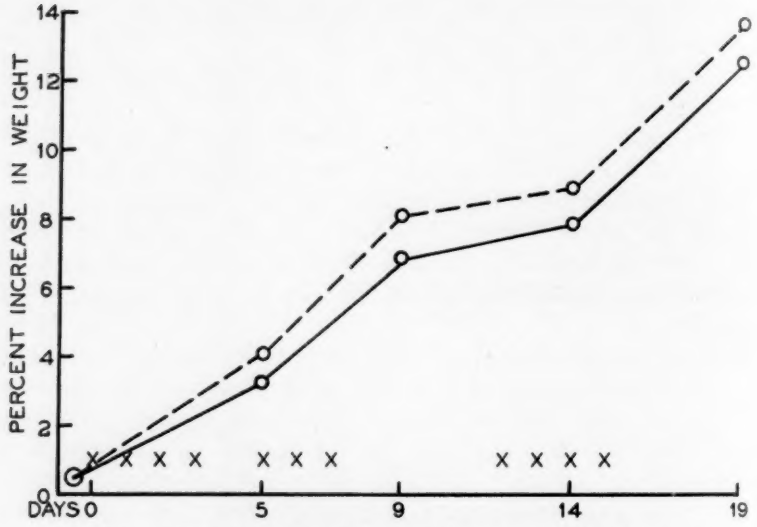

FIG. II EFFECT OF INTRAVENOUS INJECTION OF GGS ON THE GROWTH OF YOUNG RATS.

—— INJECTED WITH 0·85% SODIUM CHLORIDE SOLUTION
— — INJECTED WITH GGS SOLUTION
X INDICATES THE TIME OF INJECTIONS

When killed on the 19th day of the experiment, there was no evidence of injury produced by the injections of GGS. Microscopic examination of sections of the liver, spleen, kidney, heart and lungs of animals of the 2 groups did not reveal any lesions that could be attributed to the injections of GGS solution.

Previously, two other similar experiments had been attempted but an epidemic of colds affected most of the rats.

However, microscopic examination of the organs failed to suggest any injury-producing potentialities of GGS.

In a third experiment, growing rats were placed on a restricted diet, and one-half of them given, intravenously, daily injections of 2–3 cc. of GGS, the others an equal amount of 0.85 per cent. sodium chloride solution. Fig. III shows

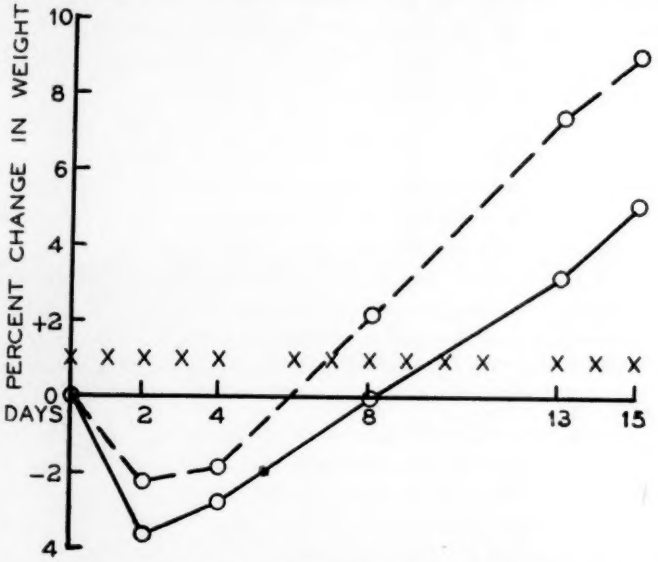

FIG. III EFFECT OF INTRAVENOUSLY INJECTED GGS ON THE GROWTH OF RATS ON A RESTRICTED DIET.

—— INJECTED WITH 0.85% SODIUM CHLORIDE SOLUTION
— — INJECTED WITH GGS SOLUTION
X INDICATES THE TIME OF INJECTIONS

the growth curves of these rats. It may be seen that those in the group which received the injections of GGS maintained their weight somewhat better than did the saline injected ones. The difference, perhaps, is not sufficient to indicate that the solution was utilized for growth; however, there is no indication that the injections were injurious to the rats.

GGS solution was found to be non-hemolytic *in vitro* to rabbit erythrocytes in concentrations ranging from 4 to 100 per cent. over a period of 12 hours.

In the burn experiments a total volume of 60 to 64 cc. of the GGS solution was the maximum injected into a rabbit during an experimental period of 6 to 7 hours' duration. In order to determine whether rabbits would tolerate larger amounts of the solution 6 injections of 30 cc. each were given to a rabbit weighing 2794 grams in a period of 7 hours. The rabbit showed no symptoms of distress during the injections or thereafter. Given in the same proportion by weight a man weighing 170 lbs. would receive 4972 cc. of the solution containing 136.4 grams of gelatin in a 7 hour period.

RESULTS.

The effects of intravenous injections of serum, 0.85 per cent. sodium chloride solution, and GGS solution on the hemoconcentration of burns are shown graphically in Fig. I. The hemoconcentration resulting after inflicting the burns is expressed by the percentage increase in the erythrocyte count, using as the basis for the calculations the count just before inflicting the burn. The difference between the height of curves representing the treated animals and the control group curve is a measure of the effectiveness of the treatments given. It may be seen that GGS and blood serum were equally effective in combatting the hemoconcentration while 0.85 per cent. sodium chloride alone had no apparent effect.

BOOK REVIEWS.

WATER-WHITE HYDROCARBONS FROM TRINIDAD ASPHALT, by Halley Tansley Gaetz. 284 pages, charts, patent applications, general discussion, 14 × 20 cms. Los Angeles, Grafton Publishing Corporation, 1937.

Determination of hydrocarbon series present in any asphaltum has been considered a problem of great magnitude. This book is a contribution in this work with respect to Trinidad Lake asphalt. It is divided into three reports, the first of which describes the process of preparation, the purpose being to purify to a water-white condition as quantitatively as possible, the petrolene hydrocarbons extracted from a sample of the commercially refined asphalt, with a view to their later commercial possibilities, including certain by-products of the process. Use is made of the selective solvent action of petroleum ether upon asphalts. The bitumen is roughly cut into three major parts by vacuum distillation, and the cut oils are individually acid-refined so as to remain water-white for a period of over two years. In reducing the sulphur content to the merest trace, a dilution process in refining heavy bitumen is featured, digestion over metallic sodium, a simple iron chain distilling column, and the use of low vacuum distillation pressures to prevent decomposition of the original stable hydrocarbons present in the extracted bitumen.

The second report gives an account of the method and principles adhered to in one fractionation vacuo of the oil portions into twenty-five small fractions. It also briefly discusses a few possibilities associated with a peculiar phosphorescent violet vapor phenomenon occurring coincidentally with the separation of paraffin wax at a temperature of approximately 260 degrees C. in vacuo. A detailed property and analytical study is given, in the third report, upon the twenty-five hydrocarbon fractions to ascertain with advanced methods the efficiency of the purification process and simple fractionation in determining the hydrocarbons and hydrocarbon series present.

The book also contains discussions and patent applications made by the author. Accompanying the book is a later patent applications pamphlet. The book contains a comprehensive subject and author index. It should be of interest to those having refining problems.

R. H. OPPERMANN.

CHEMICAL ENGINEERING CATALOG 1942–43, The Process Industries' Catalog. 1336 pages, illustrations, 22 × 28 cms. New York, Reinhold Publishing Corporation, 1942.

This twenty-seventh annual edition of the Chemical Engineers Catalog has met the urgent need for concise, accurate information, which would be of tremendous value to those interested in chemical and engineering fields. It is divided into three sections. The first covers a wide variety of equipment—up-to-date, well illustrated and complete. The second is composed of manufacturers' catalogs and a classified index of chemicals and raw materials. The last section is a list of 2500 technical books. This catalog is designed mainly as

a reference book and will find its most useful place as a handbook for chemical engineers, factory managers, chemists, operating executives, and purchasing agents, with an eye toward modern ideas.

S. T. CASSARD.

READING AS A VISUAL TASK, by Matthew Luckiesh, D.Sc., D.E., and Frank K. Moss, E.E. 428 pages, illustrations and diagrams, 14 × 22 cms. New York, D. Van Nostrand Company, Inc., 1942. Price $5.00.

Of the tasks requiring vision at close range, reading may be representative. It is a necessary task for modern work and living and, as in cases of other activities, the organs of the body must become adjusted to a different situation than that for which they were originally intended. Of late, human progress has been so rapid that the visual organs could not possibly keep in step, hence the large number of visual inefficiencies and evident casualties of different degrees. The same method which has been used to make human progress may now be used to reduce or even eventually to eliminate the penalties of change. There must be a recognition and an appraisal of all the factors having bearing on the use of vision in reading, the accomplishment of which is the object of this book.

The opening chapter is descriptive of the task of reading generally, the difference between visibility and readability, methods of obtaining data and a discussion of results. Then the construction of the eye is examined and, from this viewpoint, aids to seeing are discussed which are more or less immediately controllable. Most of these are physical aids such as eyeglasses, size of detail, contrasts, lighting, etc. Certain spurious or questionable aids to seeing which have been advocated are mentioned. A visibility meter is described in chapter three and it is shown that, when used wisely within its limitations, it provides valuable measurements of extensive import and application. From here on the book is devoted in more detail to readability factors. Visibility is taken as a basic visual attribute from which comes readability, which is descriptive of the art of reading. The factors given special attention are size of type, type-face, leading and line-length, papers and inks, and various duplicating materials.

Under the heading, "Visual Efficiencies and Deficiencies," there is discussed some amazing statistical data giving causes and suggestions for correction which provides background for the discussion of certain controllable environmental characteristics, both favorable and unfavorable, which influence the performance of the task of reading.

The authors have studied various physiological effects of seeing, not from the viewpoint of physiology, but chiefly for the purpose of establishing appropriate and sensitive criteria of ease of seeing. There are discussed researches comprising a continuous series covering the past 35 years which have evolved into the study of what is termed psychophysiological effects of seeing, most of them aimed to determine what happens as the reader reads material of various degrees of visibility, rather than why it happens. Such topics as nervous muscular tension, the heart-rate, rate of involuntary blinking, etc. are covered. Finally there is given a summary of the closing part of each chapter of the book and it is entitled "Specifications for Optimum Readability."

There are, in the back of the book, a glossary of technical terms, specimens of type and typography, a list of references to other works, and a subject index.

The book contains many illustrations in the way of photographs, diagrams, charts, and curves.

The material is well presented and easily readable. There are very few parts of the book which go to any extent into technical details and all can be understood with a minimum of effort. The book is an effective tool for the betterment of eyesight, to be used by those responsible for the preparation of reading material.

R. H. OPPERMANN.

SCIENCE REMAKES OUR WORLD, by James Stokely. 298 pages, illustrations, 15 × 23 cms. New York, Ives Washburn, 1942. Price $3.50.

Not so many years ago, expenditures of money, time, and talent for research of the nature which seemed to hold no promise of successful commercialization were seriously questioned. The fact that there was an extension of knowledge into the previously unknown was cast aside because it was impractical. As a result of this, it was claimed that research was controlled by desires of personal gain and that "pure research" flourished in countries and under conditions where the economies of the situation played little or no part. Now, all this is changed and the assertions are seldom if ever heard. So much has come from what used to be termed "pure research" that industrial concerns are spending tremendous sums in it. Its products are only beginning to appear and already have a profound effect on the life of the common man. This book has for its purpose the telling of the story of the more important of the scientific developments.

The chapters of the book coincide with the author's divisions of his subject. They cover explosives, fuels, plastics, textiles, rubber, chemurgy, medicines, vitamins, metals, products from the ocean, glass, aviation, matter, radio, light and others. A great deal of time, knowledge and experience was employed in giving the reader a readable and an interesting account of a wide variety of scientific processes heretofore understandable only to the specialist. In fact the most valuable feature of the book is its expert translation from scientific language to that which we all can comprehend. An example of this is the explanation of frequency-modulated radio broadcasting, a development probably on the threshold of general application because of its many advantages. A knowledge of it will stand everyone in good stead.

The author uses every means to give his discussions appeal and make them impressive. The story is one of action throughout. A great many branches of science are covered, reflecting an exhaustive search and broad knowledge. The work is first of all an informative story book. Second, it is a good general reference book made possible by the excellent name and subject index in the back. In view of the scientific contributions to the world from now on, this book is an essential tool to the well-informed person.

R. H.OPPERMANN.

THE AMERICAN ANNUAL OF PHOTOGRAPHY, by Frank R. Fraprie, F.R.P.S. and Franklin I. Jordan, F.R.P.S. Volume 57, 240 pages, illustrations, 19 × 25 cms. Boston, American Photographic Publishing Co. and London, Chapman & Hall, Ltd., 1942. Price $1.50.

This volume 57 is a most attractive work from many angles. To the photographer it has great appeal, particularly in the articles it contains. There are

articles on home portraiture, equipment in theory and practice, lighting for color portraiture and infrared pictorialism. A good cross section of modern thought on these as well as other subjects is given. Of course, as in every work of this kind, the photographs draw wide attention. In this number there is contained about every type of photograph. There are angle shots, close-ups, portraits, scenery, figure studies, and animal life. Not only the photographer but everyone will be interested in this. In the back there is a section on who is who in photography 1941–42, which comprises a list containing the exhibition record for the past three years of photographers who have had prints accepted by two salons within the current exhibition year. The listing includes salons open between July 1, 1941 and June 30, 1942 and assigns a rating or credit figure to each name. The method of rating is more or less familiar to contestants but is explained, together with a notice that it is not expected to continue the system beyond this year.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

Popular Science Talks, Science In War, by L. F. Tice and others. 97 pages, illustrations, 16 × 23 cms. Philadelphia, Philadelphia College of Pharmacy and Science, 1942.

Chemical Engineering Catalog 1942–1943, 1336 pages, illustrations, 22 × 28 cms. New York, Reinhold Publishing Corporation, 1942.

Atoms, Rocks, and Galaxies, by John Stuart Allen, Sidney James French, John Grant Woodruff, Clement Long Henshaw, David Woolsey Trainer, Jr. Revised edition, 719 pages, illustrations, 15 × 22 cms. New York, Harper & Bros., 1942.

Heat, by James M. Cork, Second edition, 294 pages, tables and diagrams, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1942. Price $3.50.

Sell Your Photographs, by Eugene Wyble. 167 pages, 14 × 20 cms. Boston, American Photographic Publishing Co., 1942. Price $2.00.

Principles of Electronics, by Royce G. Kloeffler. 175 pages, charts and diagrams, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1942. Price $2.50.

Communication Circuits, by Lawrence A. Ware and Henry R. Reed. 287 pages, diagrams, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1942. Price $3.50.

Applied Nuclear Physics, by Ernest Pollard and William L. Davidson Jr. 249 pages, charts and diagrams, 15 × 23 cms. New York, John Wiley & Sons, 1942. Price $3.00.

CURRENT TOPICS.

Glass Fiber Insulation Used for Brass Furnace.—(*The Iron Age*, Vol. 150, No. 13.) With mica listed as one of the nation's critical materials, the Western Cartridge Co. has successfully used Fiberglas tape in place of mica as coil insulation in the primary coil of induction-type brass furnaces. The 38 furnaces of this type installed in the Western Cartridge Co. plant have a sleeve-shaped form composed of ceramic material which retains the helical flat copper coil to form a double helix composed of alternate layers of copper and Fiberglas tape. Insulation between turns in the coil is required to prevent short circuiting. It is said that the use of the Fiberglas tape insulation made it practicable to increase furnace temperatures to the point where it was possible to produce five pours of 1500 lb. each during each 8 hr. shift, whereas with the mica insulation the limit was three pours of 1500 lb. each during each 8 hr. shift—an increased production of 300 lb. per shift, per furnace. The cost of the glass fiber insulation was 50 per cent. less than the mica it replaced. The number of man-hours required to install the Fiberglas insulation was less than half that required for the installation of mica. Approximately 1000 of the induction-type furnaces are used by the large brass companies. Most of these companies follow the practice of rebuilding their own cores when such rebuilding is necessary.

R. H. O.

Deterioration of Ground Water Supply.—Means to prevent or remedy possible deterioration of the ground water supply in the Los Angeles Basin of California, important for public supplies, agricultural and war production, are being sought by the Geological Survey and local agencies. The Geological Survey reported that salty water which may have originated in the ocean, oil well brine, or industrial waste, has appeared in some wells in the Basin along its coastal edge. Developments in the Basin—a great metropolitan community, diversified industries, and large agricultural areas—are supported largely by water drawn from local wells or diverted from remote streams. Except within the City of Los Angeles, wells have been and are the principal source. During recent years the total daily draft for all uses from wells in the basin has averaged about a third of a billion gallons. With increasing draft, salty water has

appeared in some wells within the Basin and along its coastal edge. The report says that with respect to the ground water supply, therefore, three critical questions have arisen. Is the quality of the ground-water supply deteriorating gradually owing to the incursion of ocean water, oil-well brine, or industrial wastes? If such deterioration has taken place, in what degree will it continue if present rates of withdrawal are maintained? To what degree are preventive or remedial measures feasible? Local agencies and others have made available to the Geological Survey a great mass of information, including several thousand chemical analyses of well-water samples and many tens of thousands of measurements of water levels in wells. The scope and character of this information is brought out fully in a report entitled "Index of Factual Data from Water Wells on a Part of the Coastal Plain in Los Angeles and Orange Counties, California" which has been released by the Geological Survey.

R. H. O.

New Method Speeds Tests of Cotton Moisture.—Speed or the time factor, is often important when there is need for laboratory testing of materials and products used in industry. Therefore, an improvement in efficiency in such a common test as the one for moisture content of cotton, recently developed in the U. S. Department of Agriculture, may prove a welcome saving in many plants. The new test was applied by cotton technicians of the Southern Regional Research Laboratory after others had used it on cellulose, cardboard, cotton linters and wood pulp. In testing cotton and cotton textiles it is likely to replace oven-drying in measuring the moisture taken up by cotton cloth after weaving, of cotton before it is spun, and of yarn before weaving. The new method, applied in the cotton textile field by JOHN F. KEATING and WALTER M. SCOTT of the Bureau of Agricultural Chemistry and Engineering, requires no heating at all. What is known as Fischer's reagent is used to measure the water in a solution made by treating cotton or textile with synthetic methanol. The entire test requires only about 30 minutes; the oven method from 5 to 7 hours. The oven method when carefully carried out is accurate, but the quick new method is just as accurate. The scientists who developed the new use of the method have tried it on cotton and on cotton twill and broadcloth.

R. H. O.

Study Boron Rôle in Plant Life.—Ten parts in a million of anything seems too minute a quantity to make a difference. Yet, to

keep healthy and grow normally, plants need about 10 parts in a million of boron in the soil that nourishes them. If a plant does not get enough boron it may be subject to such diseases as internal "corking" of apples, "yellows" of alfalfa, "scratch" celery or "canker" of beets. On the other hand a trifle too much boron may retard plant growth, injure tissues, or even kill the plant. Such injuries have occurred from adding boron to acid, sandy soils that were previously deficient in boron. If a field is fertilized with manure that has been treated with borax or colemanite to prevent fly hatching the borax may poison the soil and injure the plants. The desirable range in boron content is narrow. Heretofore scientists have paid more attention to the poisonous effect of boron than to its importance as a plant food. Studies by U. S. Department of Agriculture on 300 soil samples showed boron in all types of soil. Soils derived from alluvium, limestone, shale, and glacial drift are likely to be high in boron, those from igneous rocks and unconsolidated sediment, low. But natural boron toxicity is unlikely except in very arid regions. Three large regions in the United States have soils that may have too little boron. These are the Atlantic and Gulf Coasts from Maine to Texas; Northern Minnesota, Wisconsin, and Michigan; and California and the Pacific Northwestern States. Elsewhere boron deficiency is unlikely except in occasional small areas of peats, mucks, or soils developed under a high water table.

R. H. O.

Gas-Tight Box Aids Virus Studies.—Research on certain virus diseases has been hampered because some viruses live and multiply only on living cells. This has made it difficult to preserve supplies of these viruses for experiment or to interchange them between laboratories for comparison studies. T. P. DYKSTRA of the U. S. Department of Agriculture and H. G. DU BUY of the University of Maryland have devised a method for preserving plant viruses for several months. It relies mainly on keeping oxygen away from the virus material. Recently it has been found practical to propagate some of the animal viruses by injecting them into eggs where they can be incubated and multiplied for use in the laboratory or to immunize animals. Many plant viruses, however, have been short lived and had to be kept alive by injecting them into a series of living plants. The essential of the new method is a gas-tight box with openings at the ends into which rubber gloves are sealed. A glass cover enables the operator to see his hands at work. By crushing infected plant material in an atmosphere of carbon dioxide, evaporating the juice in a vacuum, and sealing it in a glass tube, the

scientists preserved potato viruses for months. An air leak would inactivate the virus, confirming the opinion that oxidation was the chief cause of the early death of viruses.

R. H. O.

New-Construction Possibilities for Chemical Plants.—(*Chemical and Engineering News*, Vol. 20, No. 19.) A new and revolutionary technique in plant construction which may hold distinct advantages for chemical processing units has been developed in a joint effort by the Truscon Steel Co., Owens-Corning Fiberglas Corp., and The Austin Co. The new building method, called "Ferroglas construction," has been successfully used in two huge new plants erected and completed late last year in the Southwest. Features of this construction, which uses practically only Fiberglas and steel, are excellent insulating properties, low sound reflectivity, high light reflectivity, and, important to the chemical field, little condensation of vapor. The construction is simple, lends itself to speedy construction, and is uniform, although sidewall and roof techniques are somewhat different. Thus the wall, completely constructed from one outside scaffolding, is built up from the inside with expanded metal mesh, a Fiberglas mat, a 4 inch blanket of Fiberglas, a metal channel, a vapor seal of cold asphalt primer and vapor resistant paper, a 1 inch Fiberglas insulation board, and on the outside of the building a metal facing panel. To facilitate construction and to save time, the sidewall channel is filled at the job site with the Fiberglas insulation blanket, the retaining mat, and metal mesh. The complete, filled C-channels are then hoisted into position and secured to the connecting plates by metal screws. Roofs of Ferroglas construction are built up in layers similar to the sidewall; the chief difference is that there are no prefabricated sections such as the filled channel hoisted into place for the side wall. Expanded metal guards are fastened to the runner channels by clips, and above the expanded metal is placed a colorless, light-reflecting, Fiberglas retaining mat which prevents passage of dust but does not materially reduce the sound absorption qualities of the blanket of Fiberglas laid directly on it. These three materials constitute the ceiling of the factory. The roof proper is made of metal roof deck welded to the purlins and having on its upper side a continuous vapor seal which is mopped on. Over this seal a 13/16 inch thickness of 6 pound density Fiberglas roof insulation board is laid; finally, a built-up waterproofing, consisting of four layers of roofing paper held in place with melted pitch, is applied over that.

R. H. O.